PAUL SCHERRER INSTITUT

PSI

Wir schaffen Wissen – heute für morgen

Paul Scherrer Institut

Peter Radi

Characterization of the 1 $^5\Pi_u$ – 1 $^5\Pi_g$ band of C_2 by two-color resonant four-wave mixing and LIF

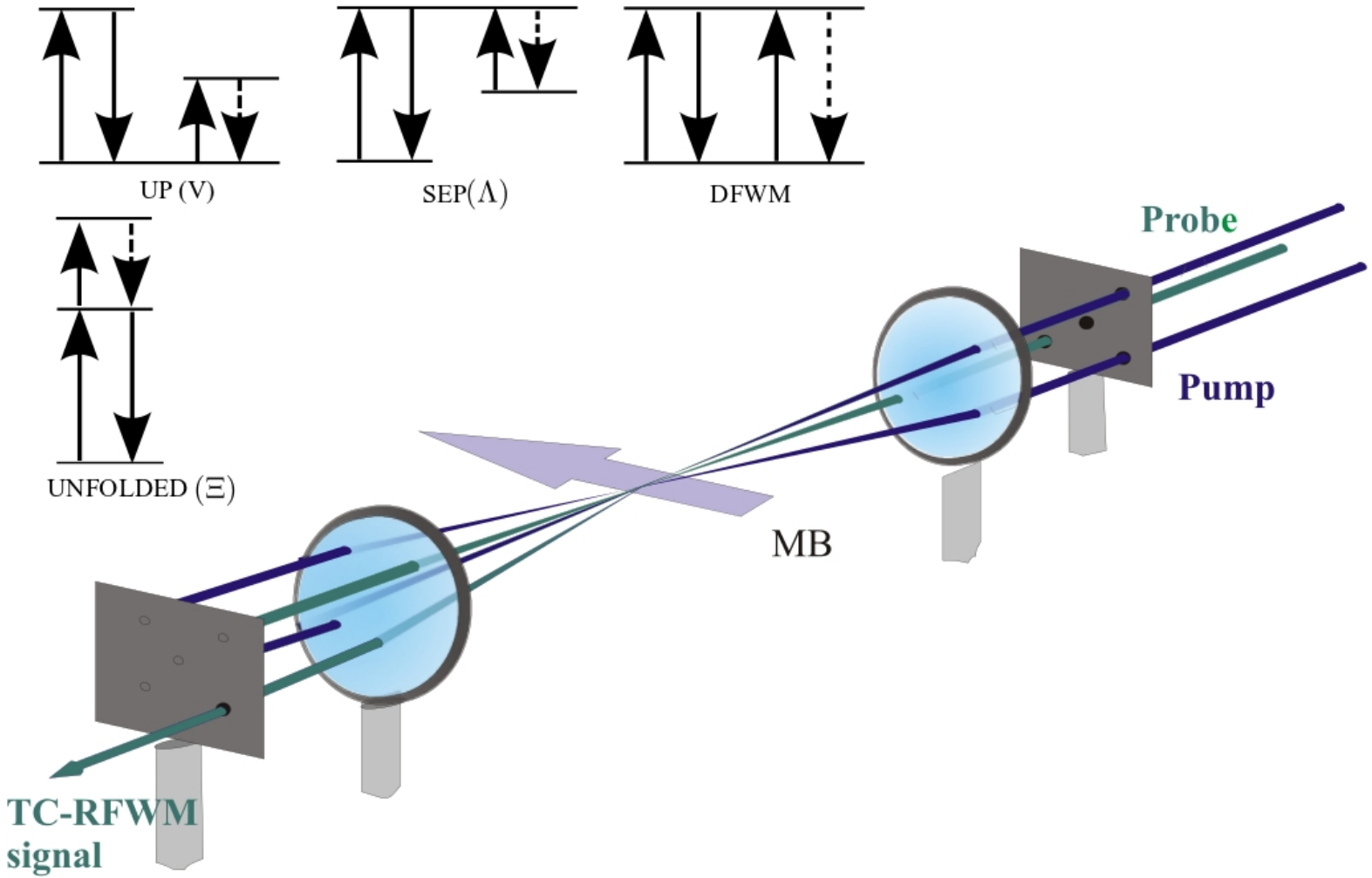
Outline

- Perturbations
- The potential of two-color resonant four-wave mixing for deperturbation studies
- Accessing the quintet manifold via “gateway states”
- Characterization of the $^5\Pi_u$-$^5\Pi_g$ electronic transition
- ab initio computations

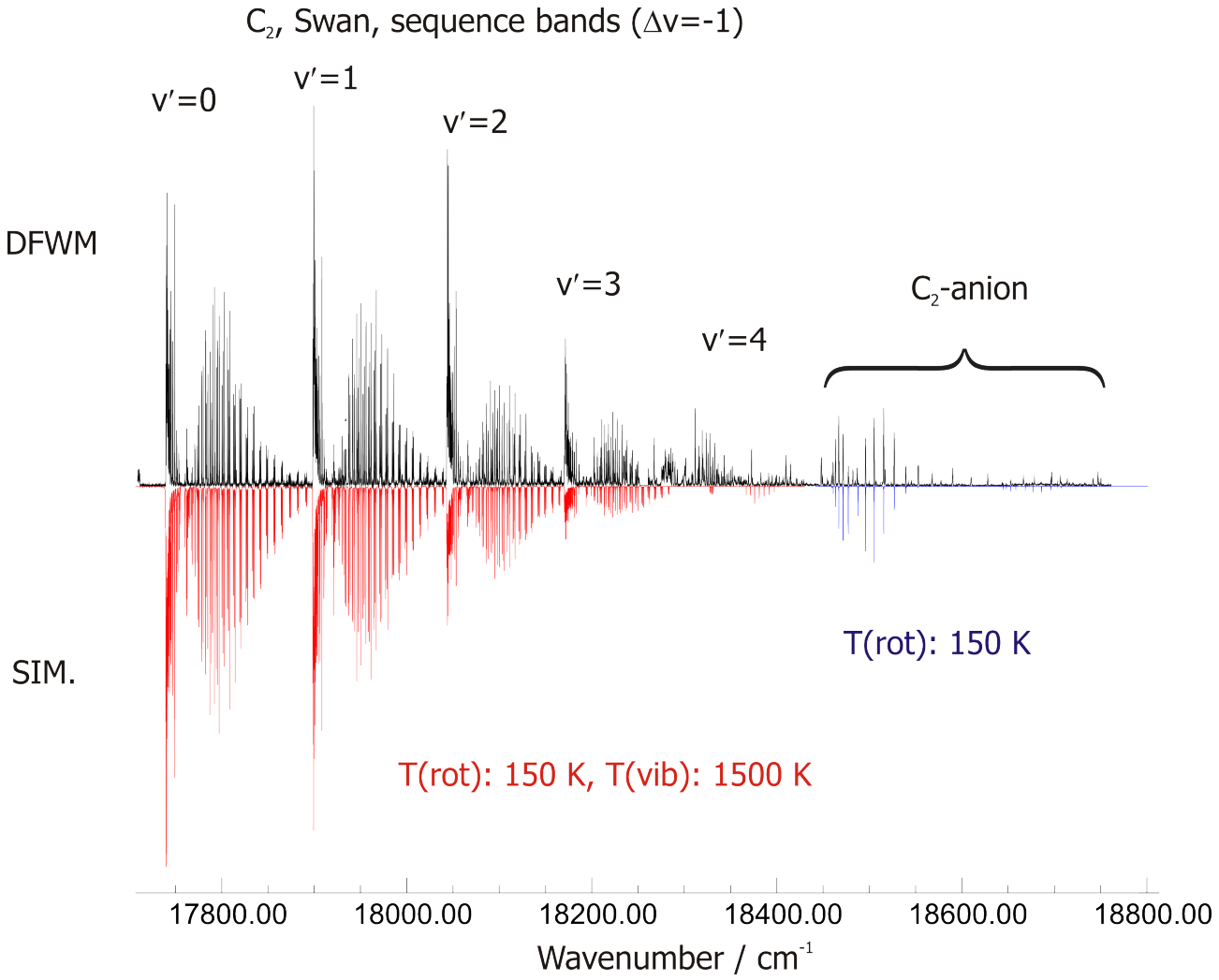
Perturbations

- Perturbation effects open ways to observe dark states (with small transitions moments) on optically more accessible bright states. The spectroscopically dark states can be dynamically active and they can play an important role in energy flow processes governing intra- and intermolecular energy redistribution

double-resonant four-wave mixing

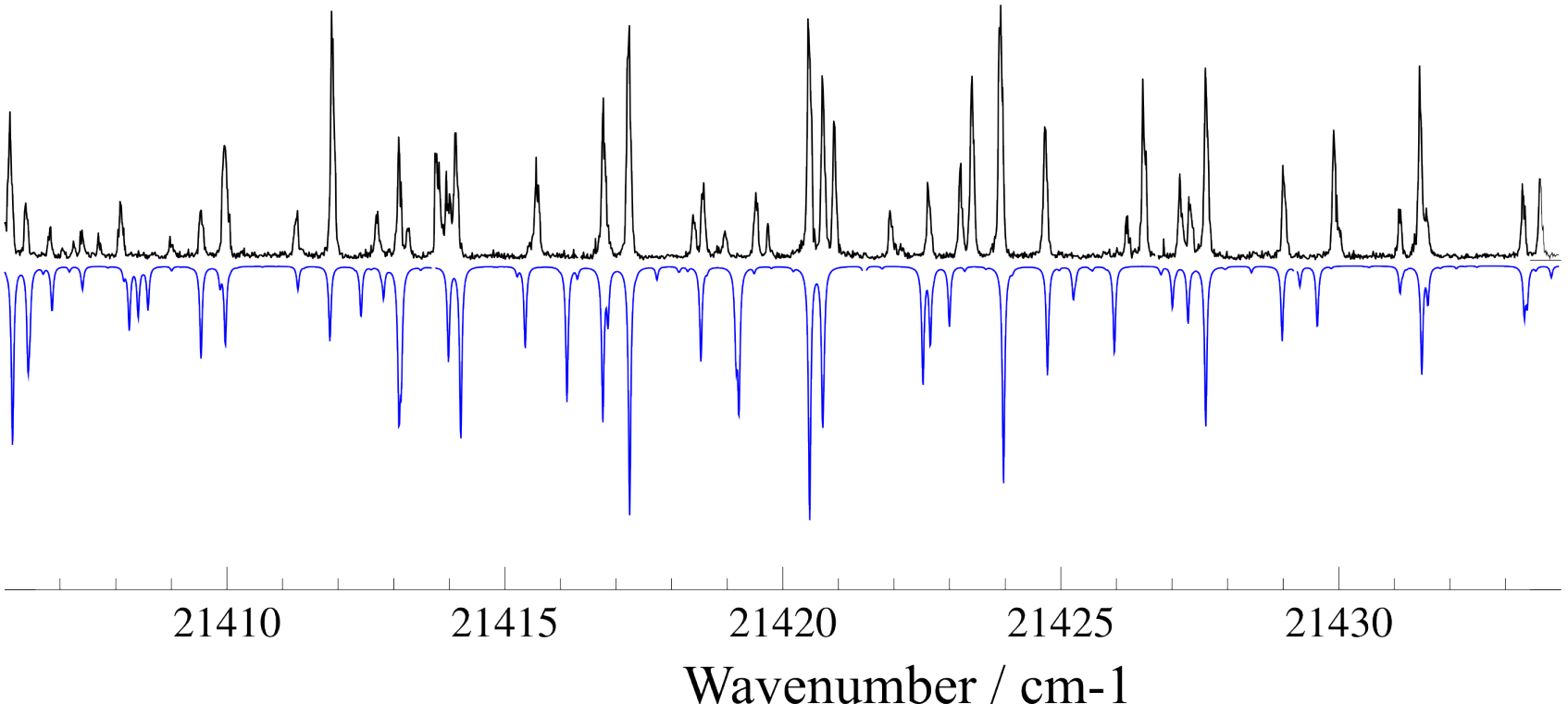


DFWM



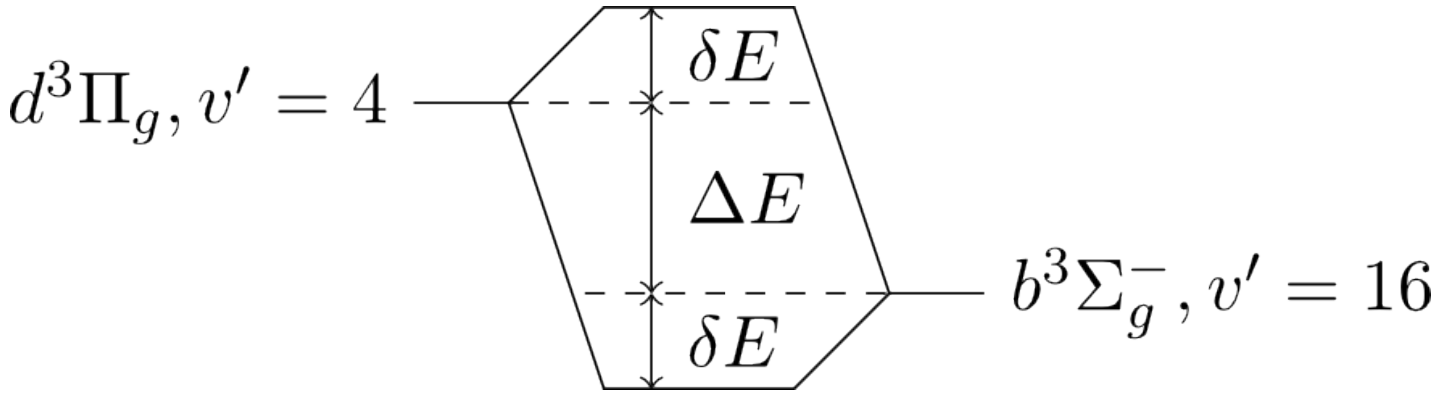
Tulej, M., Knopp, G., Gerber, T. & Radi, P.P., Journal of Raman Spectroscopy 41, 853-858 (2010).

Swan-band around 467 nm (omitting perturbation)



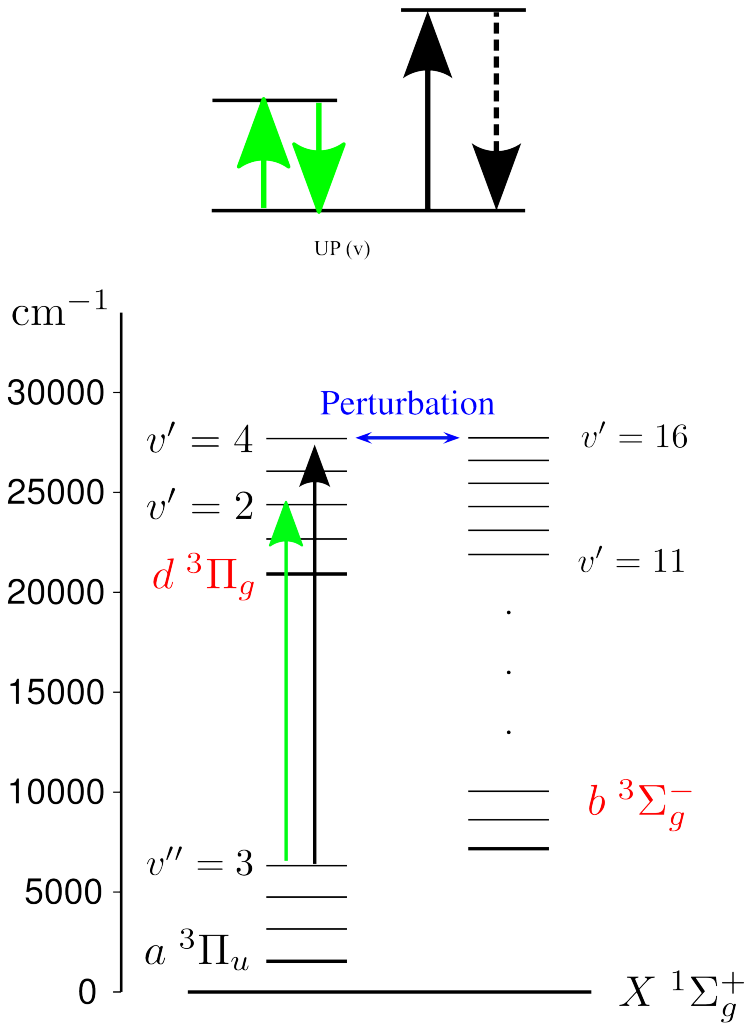
A. Tanabashi, T. Hirao, T. Amano, and P.F. Bernath, The Astrophysical Journal Supplement Series 169, 472 (2007).

Perturbation



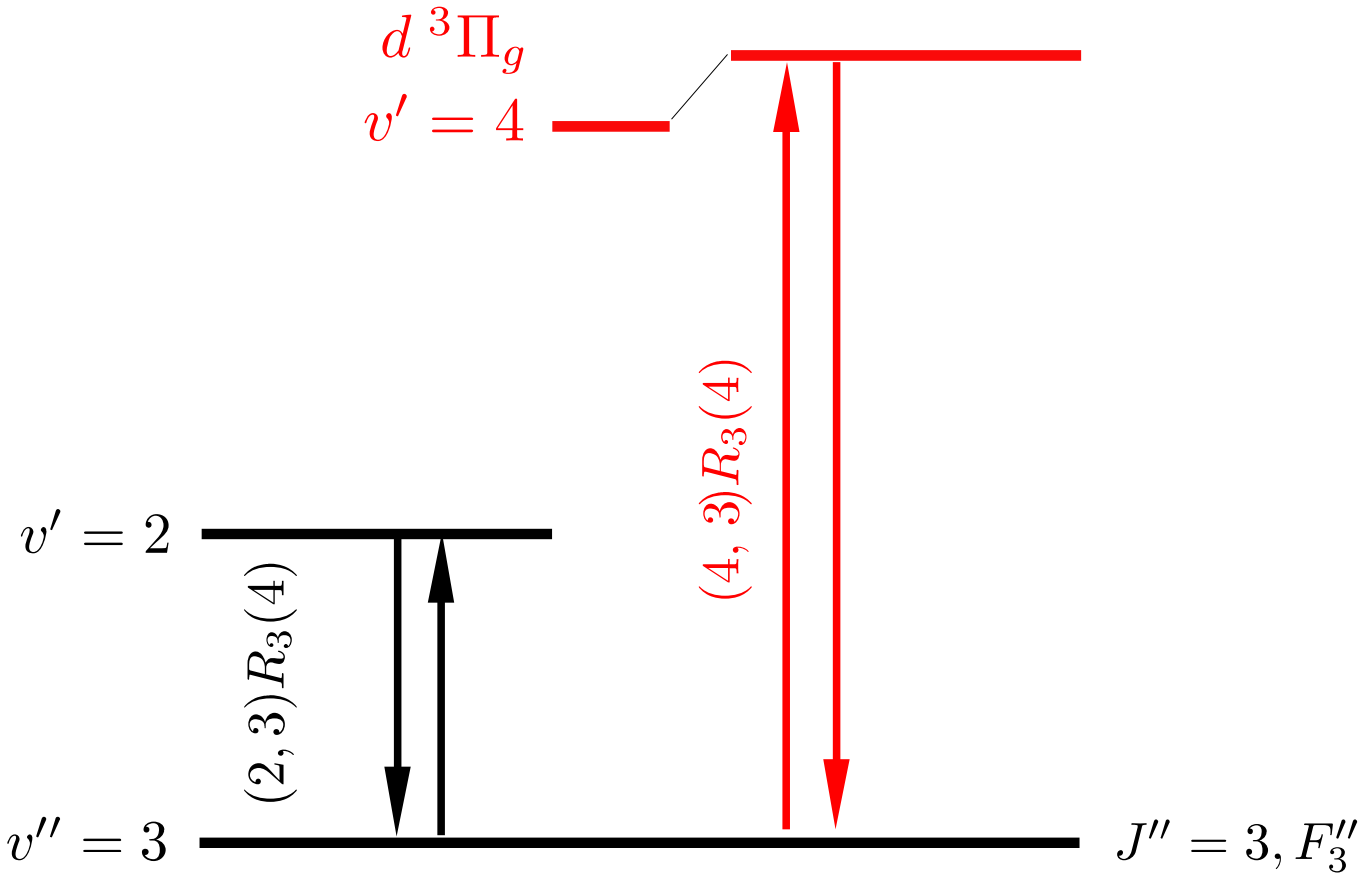
- $E = \frac{1}{2}(E_1 + E_2) \pm \frac{1}{2}\sqrt{4W_{12}^2 + \Delta E^2}$
- $\delta E = \pm\frac{1}{2}(\sqrt{4W_{12}^2 + \Delta E^2} - \Delta E)$
- The spectral separation observed between perturbed and perturbing transitions is given by $2\delta E + \Delta E$, where ΔE is the separation of the two levels in the absence of perturbation and δE is the displacement of the levels resulting from the perturbation

Example: Deperturbation of the v'=4 level

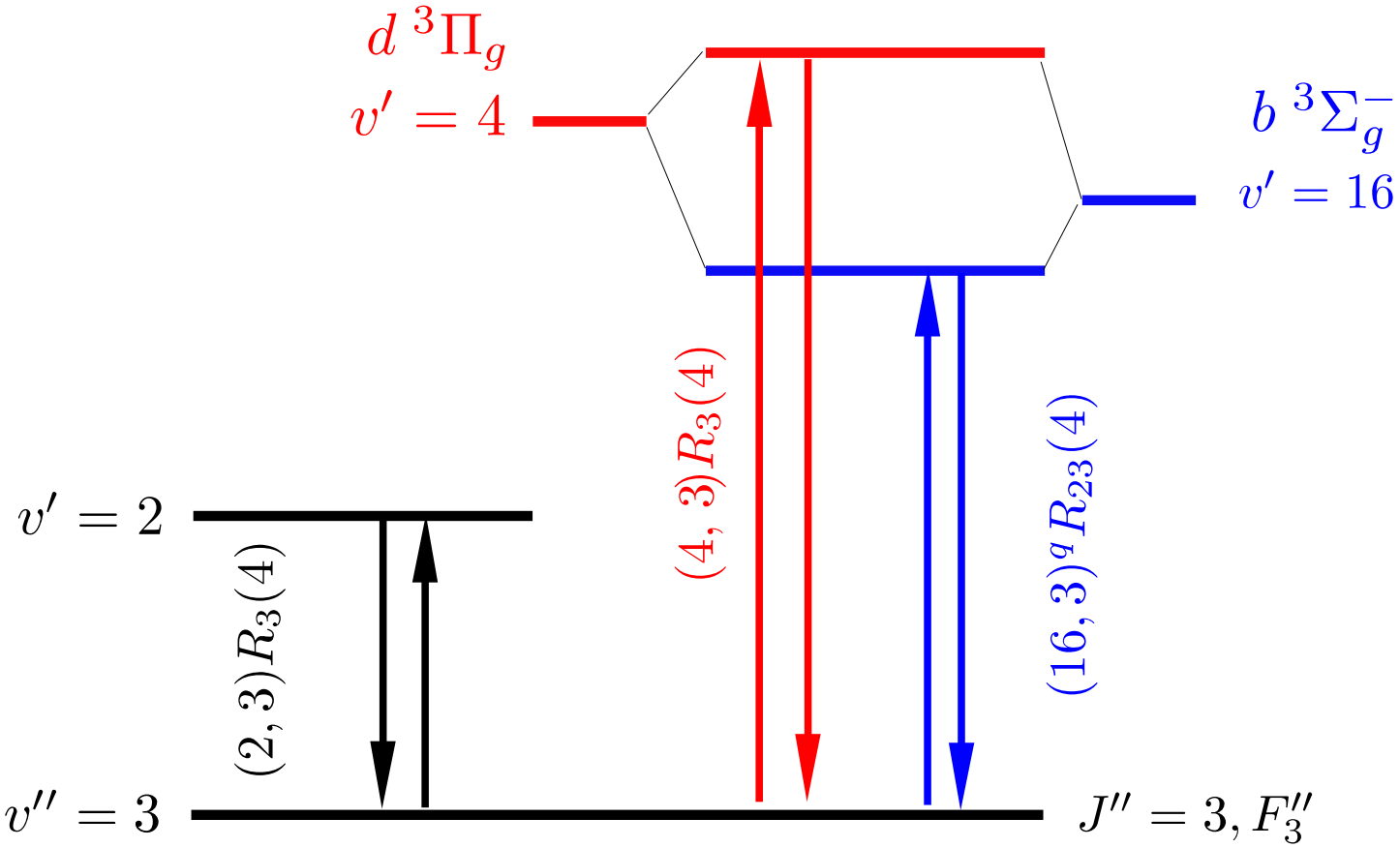


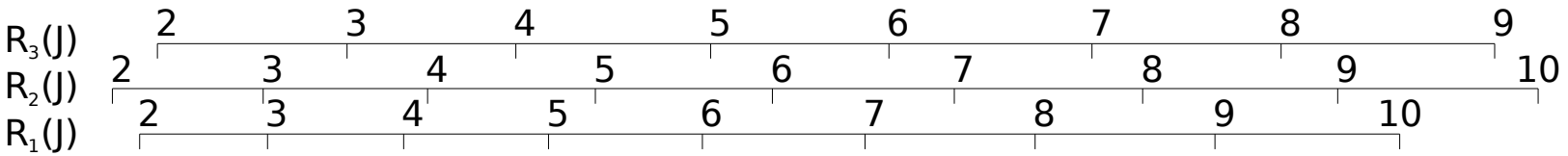
Deperturbation by TC-RFWM

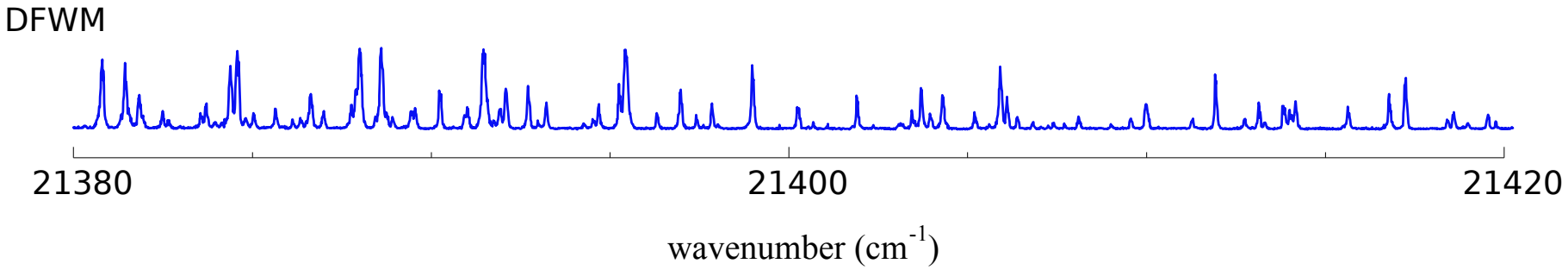
Deperturbation by TC-RFWM

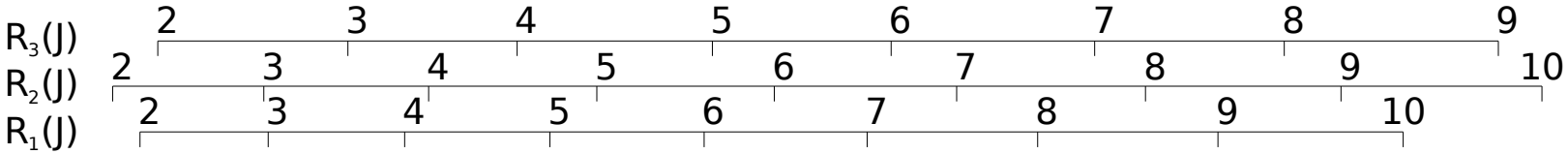


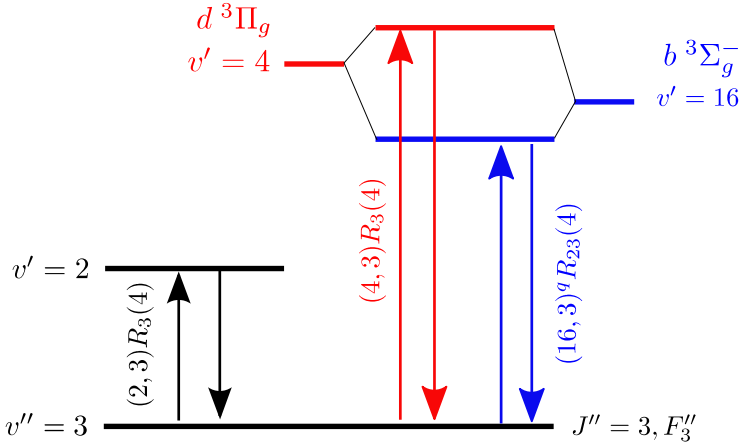
Deperturbation by TC-RFWM



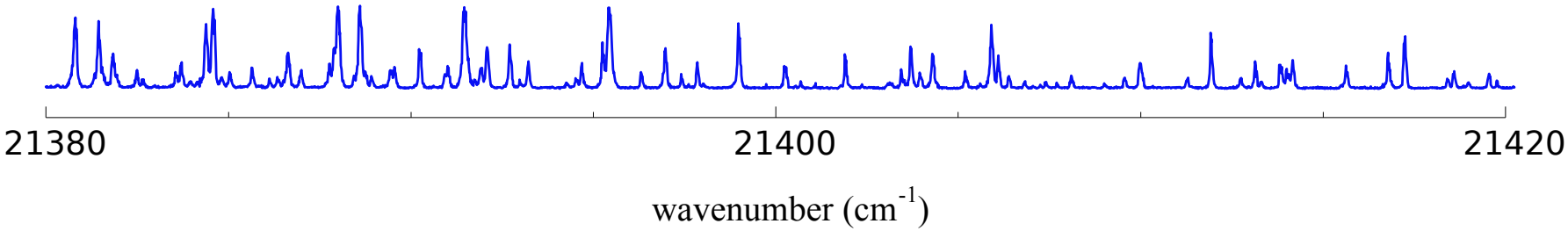

R3(J)
R2(J)
R1(J)
2 3 4 5 6 7 8 9
2 3 4 5 6 7 8 9 10
2 3 4 5 6 7 8 9 10

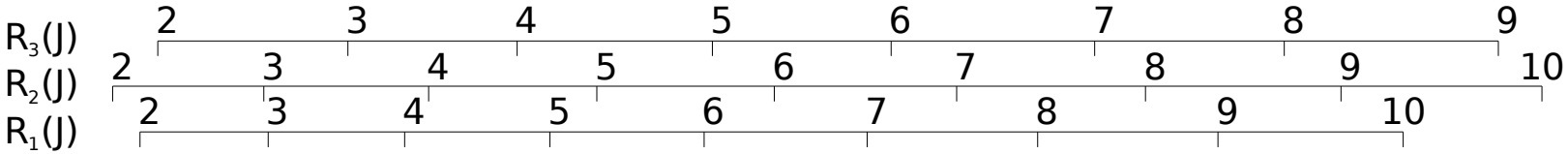

DFWM
21380
21400
21420
wavenumber (cm-1)

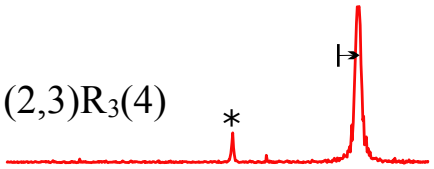

R3(J)
R2(J)
R1(J)
2 3 4 5 6 7 8 9
2 3 4 5 6 7 8 9 10
2 3 4 5 6 7 8 9 10

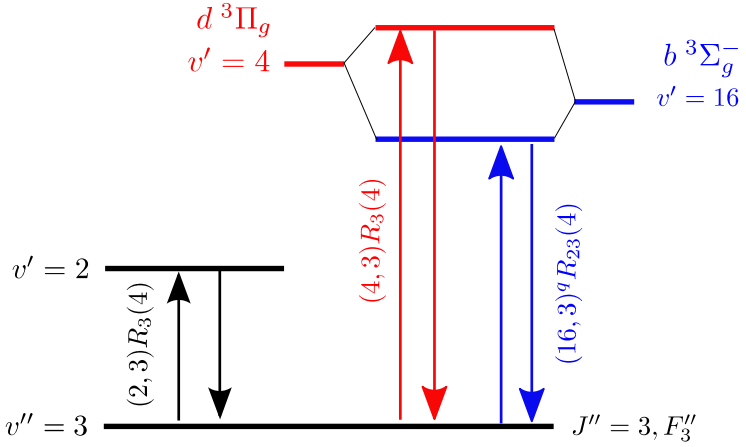

$d\ ^3\Pi_g$
$v' = 4$
$b\ ^3\Sigma_g^-$
$v' = 16$
$(4,3)R_3(4)$
$(16,3)^qR_{23}(4)$
$v' = 2$
$(2,3)R_3(4)$
$v'' = 3$
$J'' = 3, F_3''$

DFWM

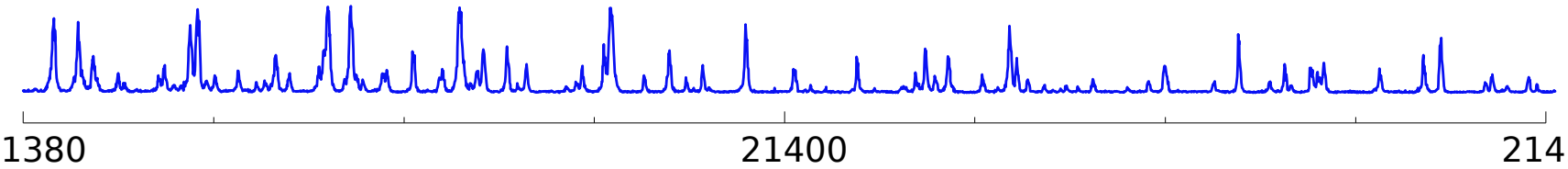

21380
21400
21420
wavenumber (cm-1)

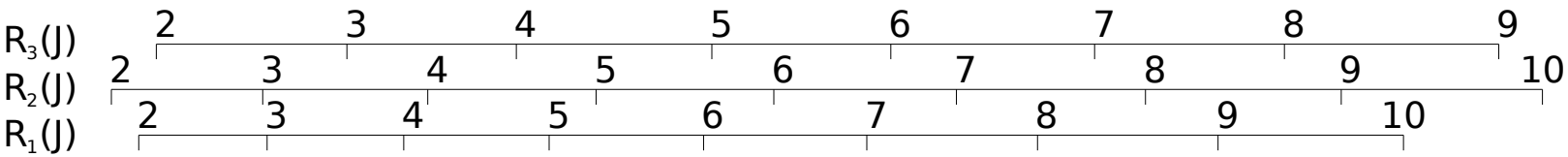

R3(J)
R2(J)
R1(J)
2 3 4 5 6 7 8 9
2 3 4 5 6 7 8 9 10
2 3 4 5 6 7 8 9 10

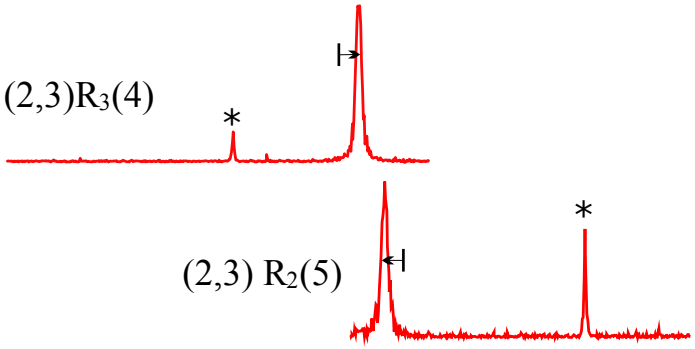

(2,3)R3(4)


d ³Πg
v′ = 4
b ³Σg⁻
v′ = 16
v′ = 2
v″ = 3
J″ = 3, F3″
(2, 3)R3(4)
(4, 3)R3(4)
(16, 3)qR23(4)

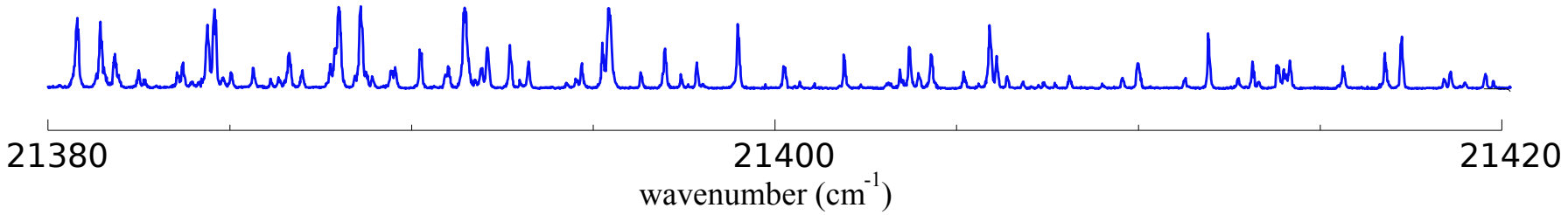
DFWM

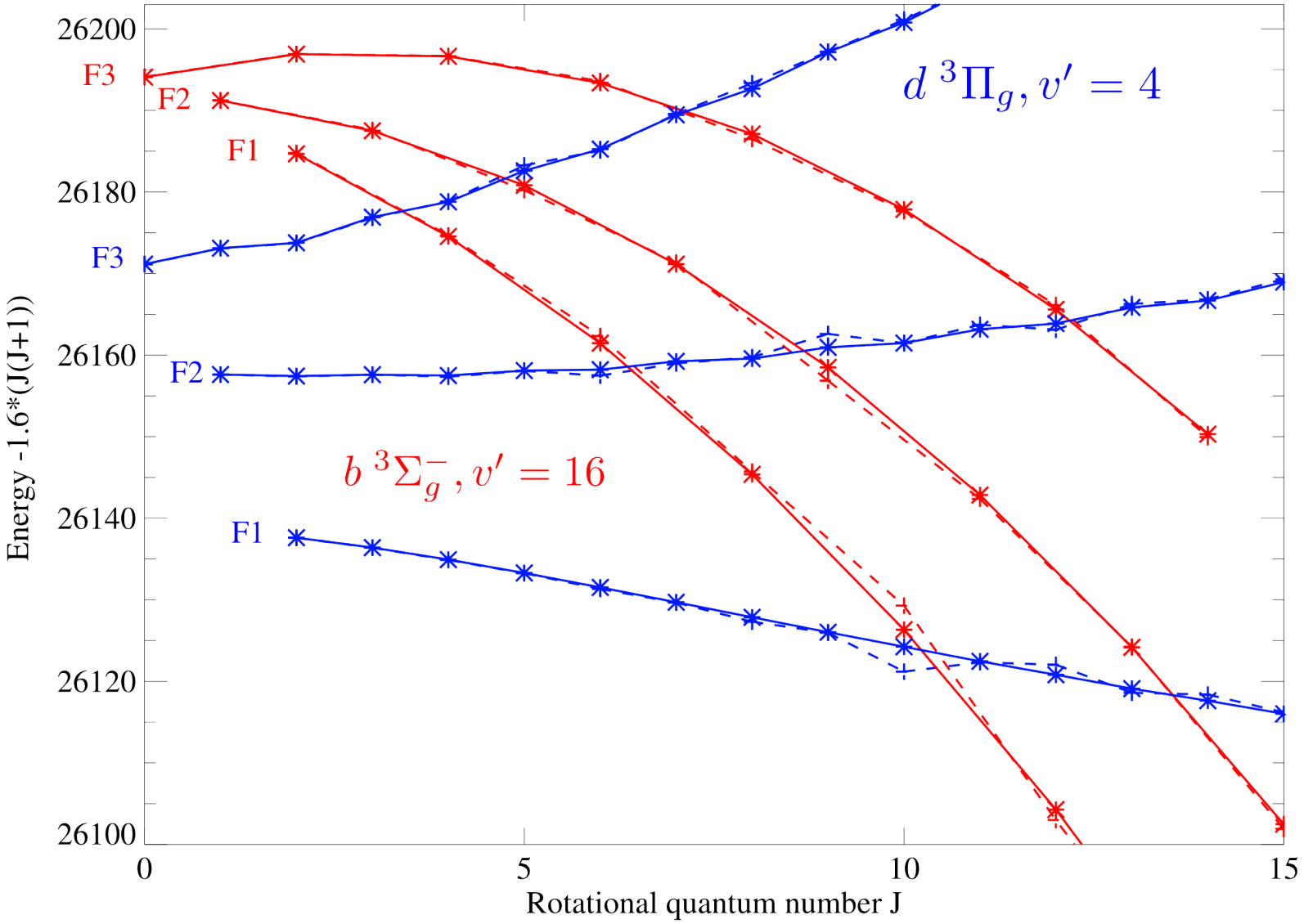

21380
21400
21420
wavenumber (cm-1)


R3(J)
R2(J)
R1(J)
2 3 4 5 6 7 8 9
2 3 4 5 6 7 8 9 10
2 3 4 5 6 7 8 9 10


(2,3)R3(4)
(2,3) R2(5)

DFWM


21380
21400
21420
wavenumber (cm-1)


26200
26180
26160
26140
26120
26100
Energy -1.6*(J(J+1))
0
5
10
15
Rotational quantum number J
F3
F2
F1
F3
F2
F1
$d\,^3\Pi_g, v' = 4$
$b\,^3\Sigma_g^-, v' = 16$

Molecular constants

Table 2
Optimized molecular constants for the perturbing $b^3\Sigma_g^-, v = 16$ state and parameters resulting from the interaction with the $d^3\Pi_g, v' = 4$ state. All values are in cm^{-1}. The origin, T, is relative to the $a^3\Pi_u, v'' = 0$ level. Numbers in parenthesis are one standard deviation.

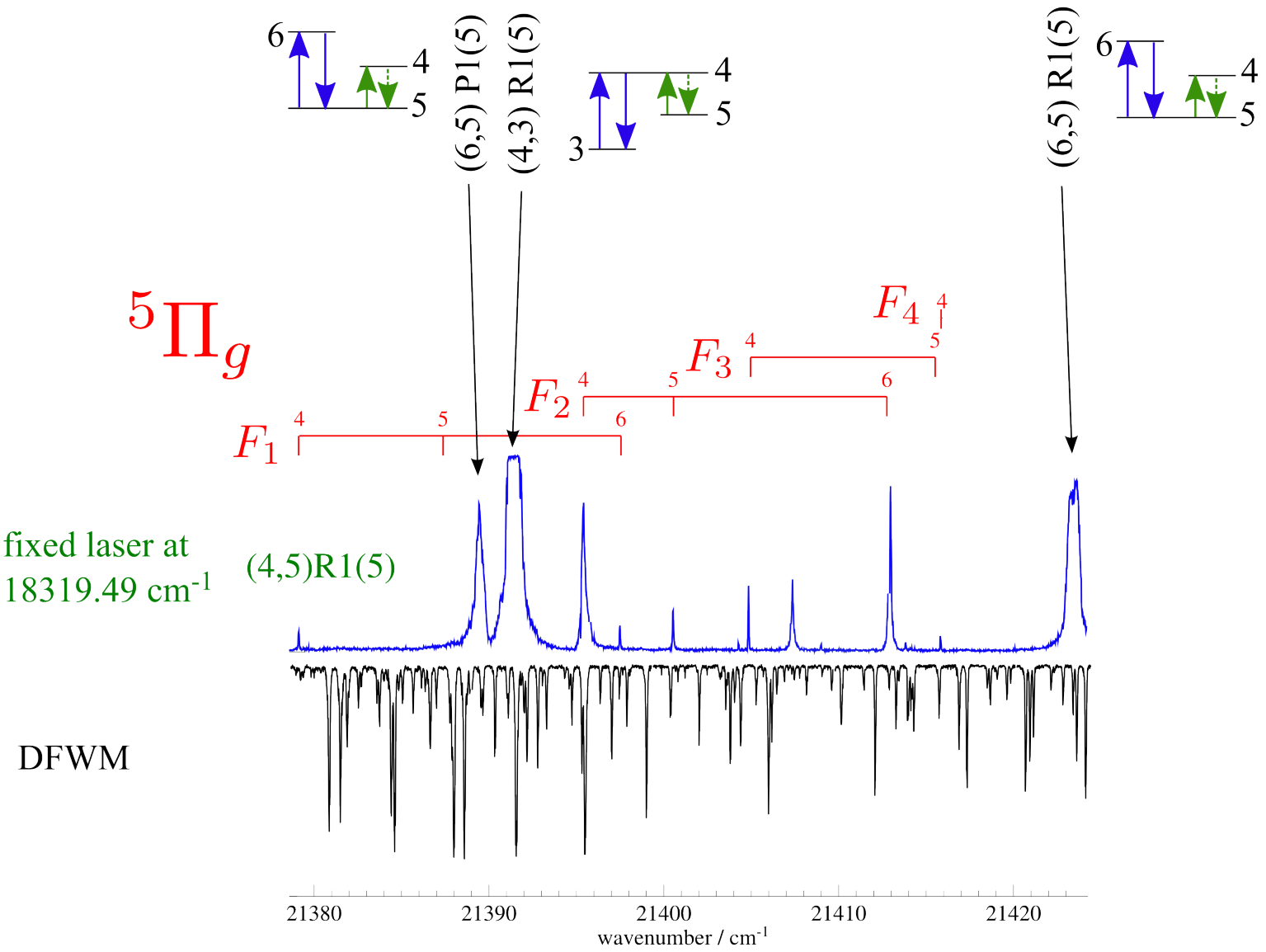
State	Parameter	Optimized w/o extra lines	Optimized value	Extrapolated[a]
$b^3\Sigma_g^-, v' = 16$	T	26192.081(72)	26191.865(14)	26187.074
	B	1.22508(98)	1.22858(15)	1.22824
	$D \times 10^6$	6.4351[b]	6.4351[b]	6.4351[b]
	λ	0.32(11)	0.172(18)	0.155
$\langle d^3\Pi_g, v' = 4 \vert \mathbf{H}_{SO} \vert b^3\Sigma_g^-, v' = 16\rangle$		−0.6120(167)	−0.6401(86)	
$\langle d^3\Pi_g, v' = 4 \vert B\mathbf{L}_+ \vert b^3\Sigma_g^-, v' = 16\rangle$		0.2459(13)	0.24737(61)	

[a] Ref. [37].
[b] Fixed at the extrapolated value.

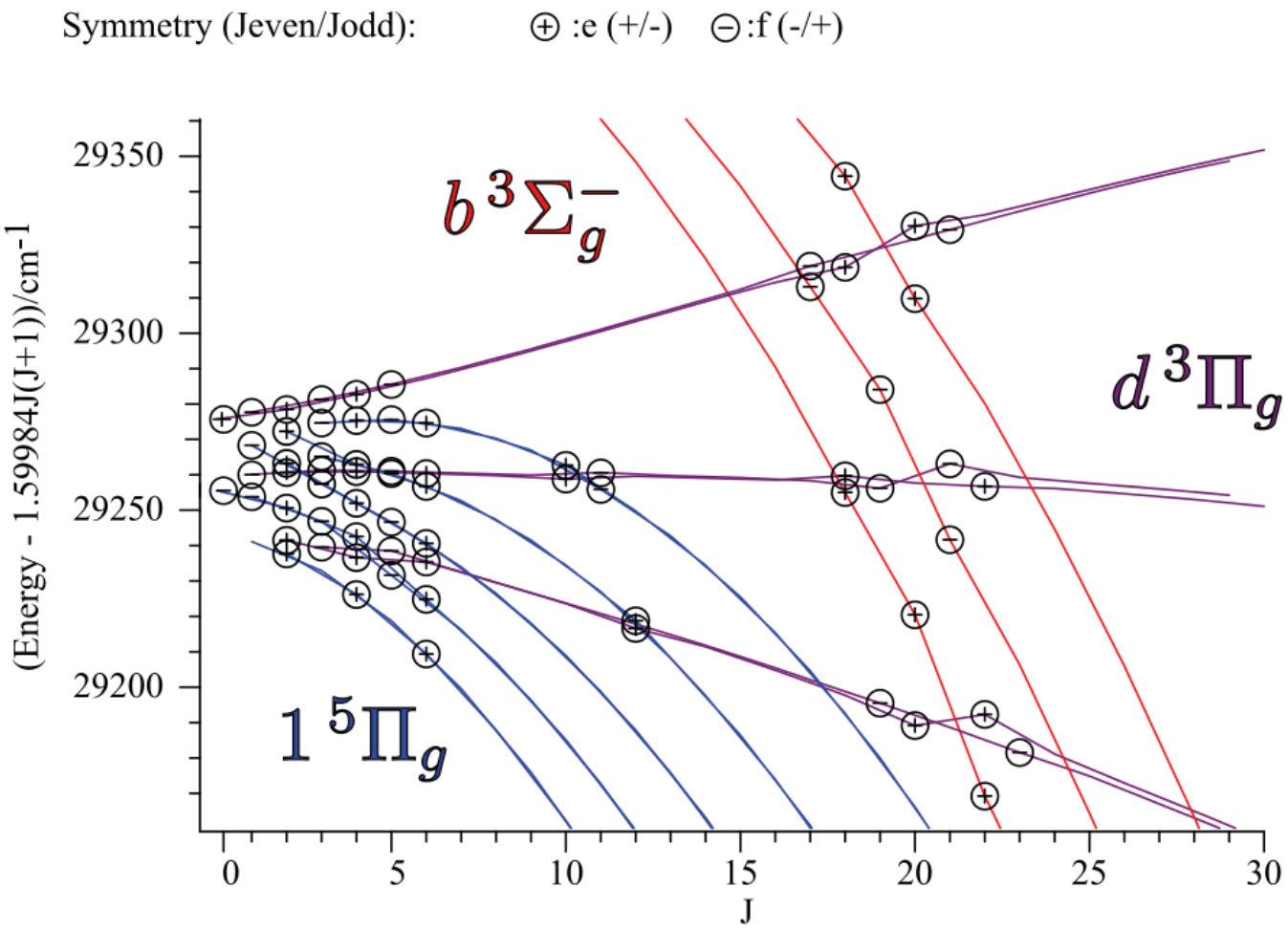
P. Bornhauser, G. Knopp, T. Gerber, and P.P. Radi, Journal of Molecular Spectroscopy 262, 69 (2010).

Deperturbation by TC-RFWM

- **Spectral simplification by intermediate level labeling** provides a powerfool tool to assign complex one-color spectra
- **High dynamic range** up to S/N of 10^9 allows observation of the extremely weak perturbing levels


6
4
5
(6,5) P1(5)
(4,3) R1(5)
3
4
5
(6,5) R1(5)
6
4
5
$^5\Pi_g$
F_4 4 5
F_3 4 5 6
F_2 4 5 6
F_1 4 5
fixed laser at
18319.49 cm^{-1}
(4,5)R1(5)
DFWM
21380
21390
21400
21410
21420
wavenumber / cm^{-1}

Measured energy levels



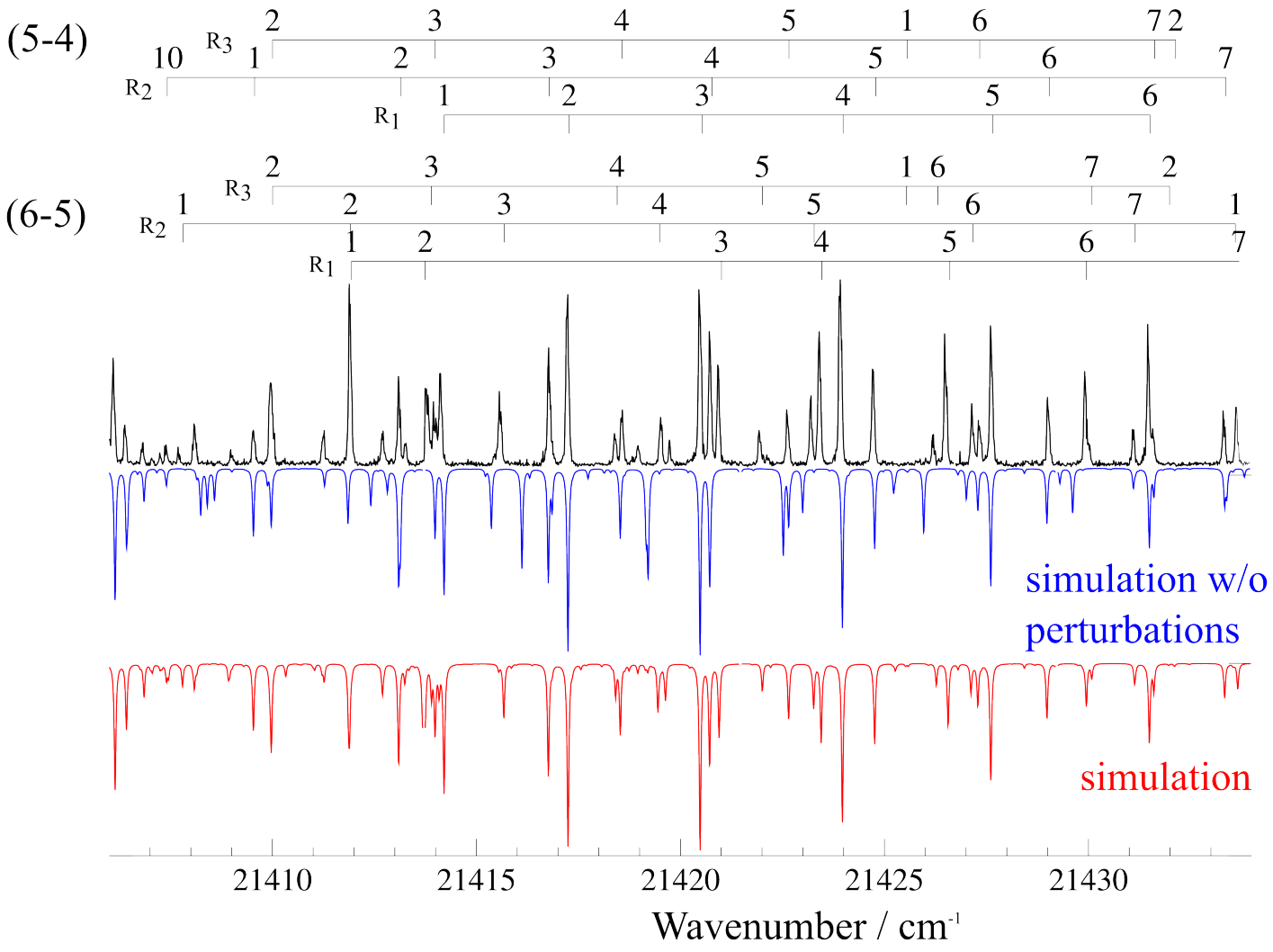
Optimized molecular parameters

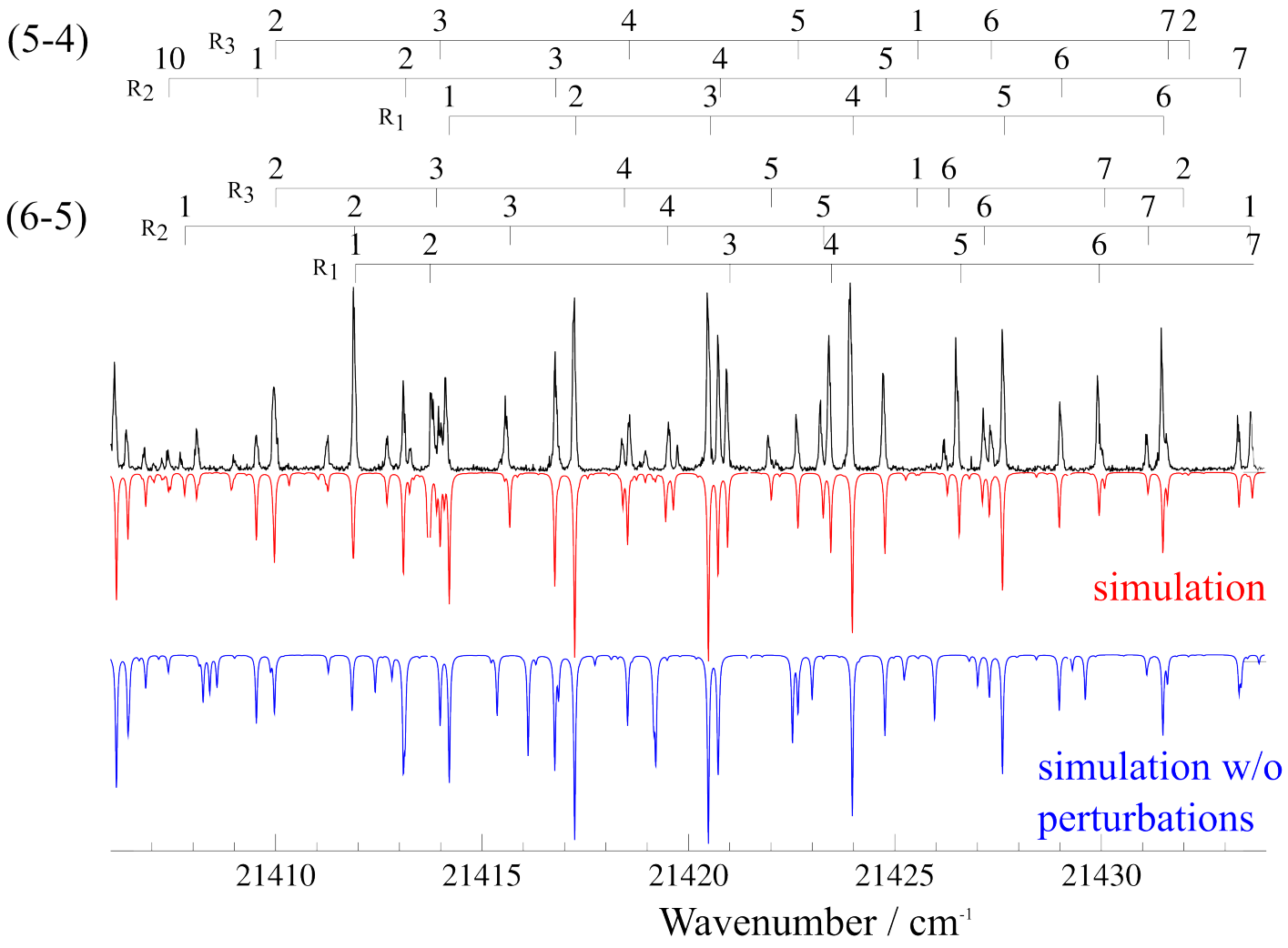
TABLE IV. Optimized molecular constants for the $1\,^5\Pi_g$, $d\,^3\Pi_g$, $v = 6$, and the $b\,^3\Sigma_g^-$, $v = 19$ states. All values are in cm^{-1}. The origin, T is relative to the $a\,^3\Pi_u$, $v = 0$ level. Numbers in parenthesis are one standard deviation.

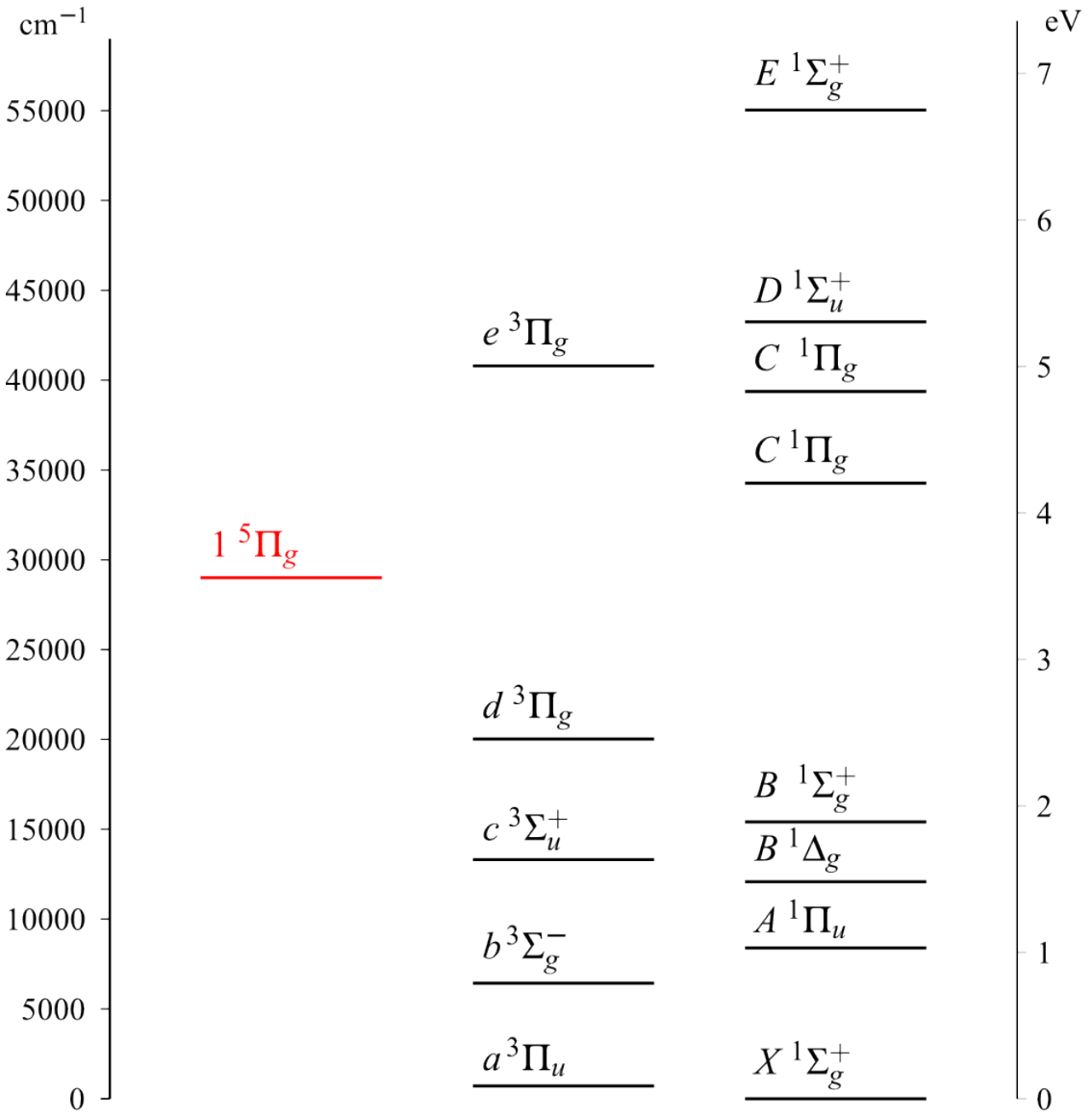
State	Parameter	Value	Reference
$1\,^5\Pi_g$	T	29258.5922(48)	29941.99[b]
	B	1.14413(11)	1.012[b]
	A	8.9450(47)	
	λ	–0.0428(23)	
	o	–0.0744(39)	
$b\,^3\Sigma_g^-$, $v = 19$	T	29442.1348(843)	29434.25[c]
	B	1.179368(214)	1.178804[c]
	D $\times 10^6$	6.5066[c]	6.5066[c]
	λ	0.142(22)	0.1548[c]
$d\,^3\Pi_g$, $v = 6$	T	29259.3736(32)	29259.704 (14)[a]
	A	–12.8223(90)	–13.082 (35)[a]
	p	0.00467(91)	0.00104(65)[a]
	q	–0.000964(44)	–0.001514(17)[a]
$\langle d\,^3\Pi_1, v = 6 \vert H_{so} \vert 1\,^5\Pi_1 \rangle$		4.6220(88)	
$\langle d\,^3\Pi_1, v = 6 \vert H_{so} \vert b\,^3\Sigma_1^-, v = 19 \rangle$		0.7855(110)	
$\frac{1}{\sqrt{x}} \langle d\,^3\Pi_0, v = 6 \vert BL_+ \vert b\,^3\Sigma_1^-, v = 19 \rangle$		0.31192(37)	

[a]Reference 17.
[b]Listed values are for $v = 0$ in Ref. 31.
[c]Extrapolated from the results in Ref. 51.

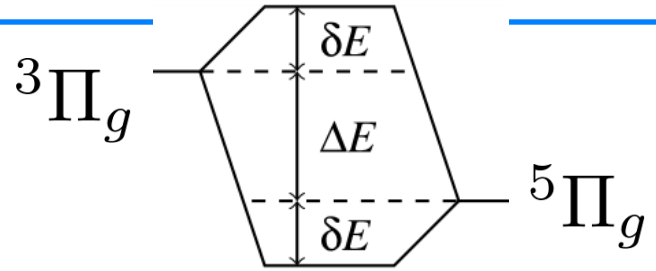
P. Bornhauser, Y. Sych, G. Knopp, T. Gerber, and P.P. Radi, J. Chem. Phys. 134, 044302 (2011).


(5-4)
(6-5)
R3
R2
R1
simulation w/o perturbations
simulation
21410
21415
21420
21425
21430
Wavenumber / cm-1


(5-4)
(6-5)
R3
R2
R1
simulation
simulation w/o perturbations
21410
21415
21420
21425
21430
Wavenumber / cm-1


cm^{-1}
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
eV
7
6
5
4
3
2
1
0
$E\ ^1\Sigma_g^+$
$D\ ^1\Sigma_u^+$
$e\ ^3\Pi_g$
$C\ ^1\Pi_g$
$C\ ^1\Pi_g$
$1\ ^5\Pi_g$
$d\ ^3\Pi_g$
$B\ ^1\Sigma_g^+$
$c\ ^3\Sigma_u^+$
$B\ ^1\Delta_g$
$A\ ^1\Pi_u$
$b\ ^3\Sigma_g^-$
$a\ ^3\Pi_u$
$X\ ^1\Sigma_g^+$

Gateway states

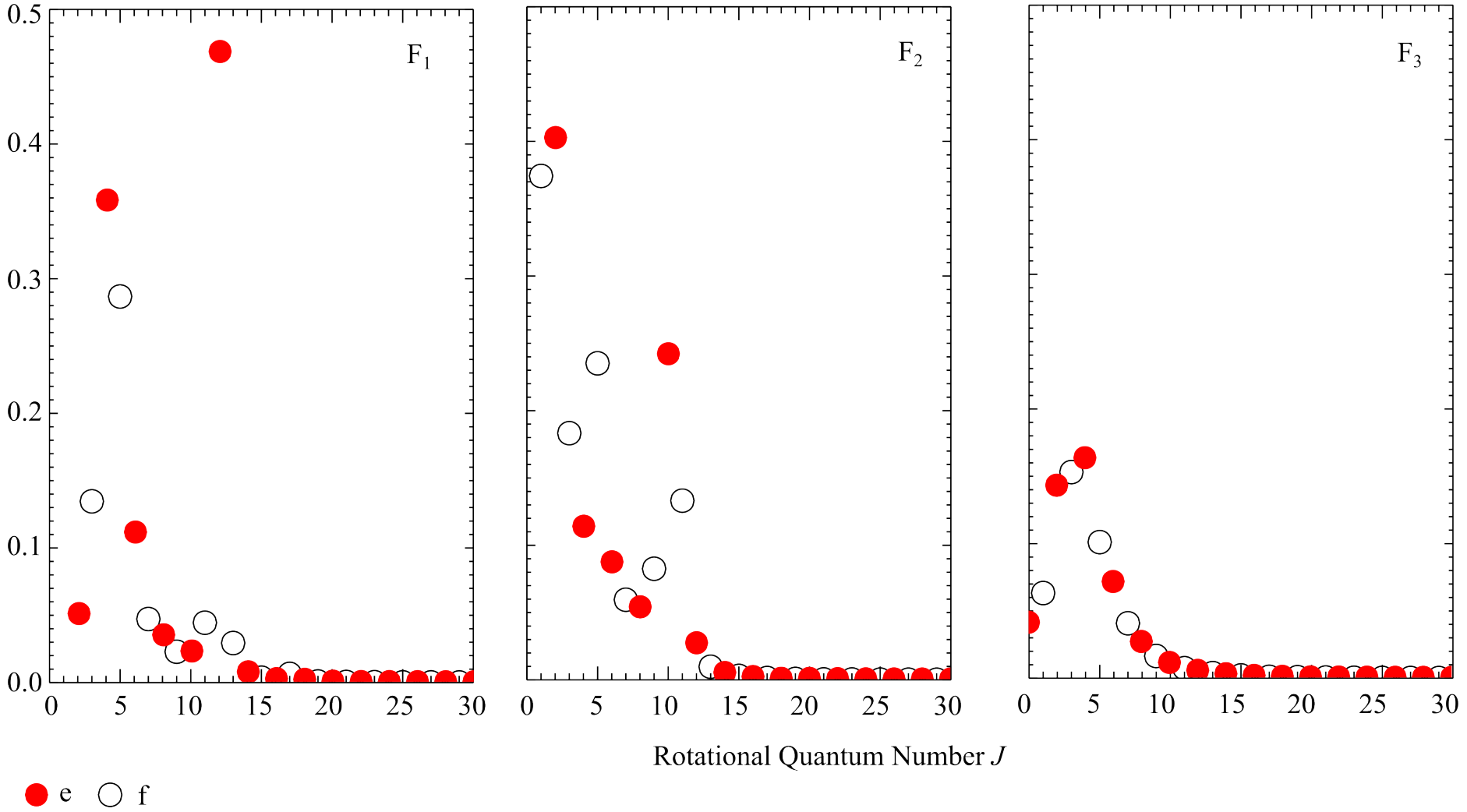


$$\sigma_{E,J;E',J'} \simeq \sigma_{E,J;E,J'} C_{E,E'} (J')^2 + \sigma_{E',J;E',J'} C_{E,E'} (J)^2$$

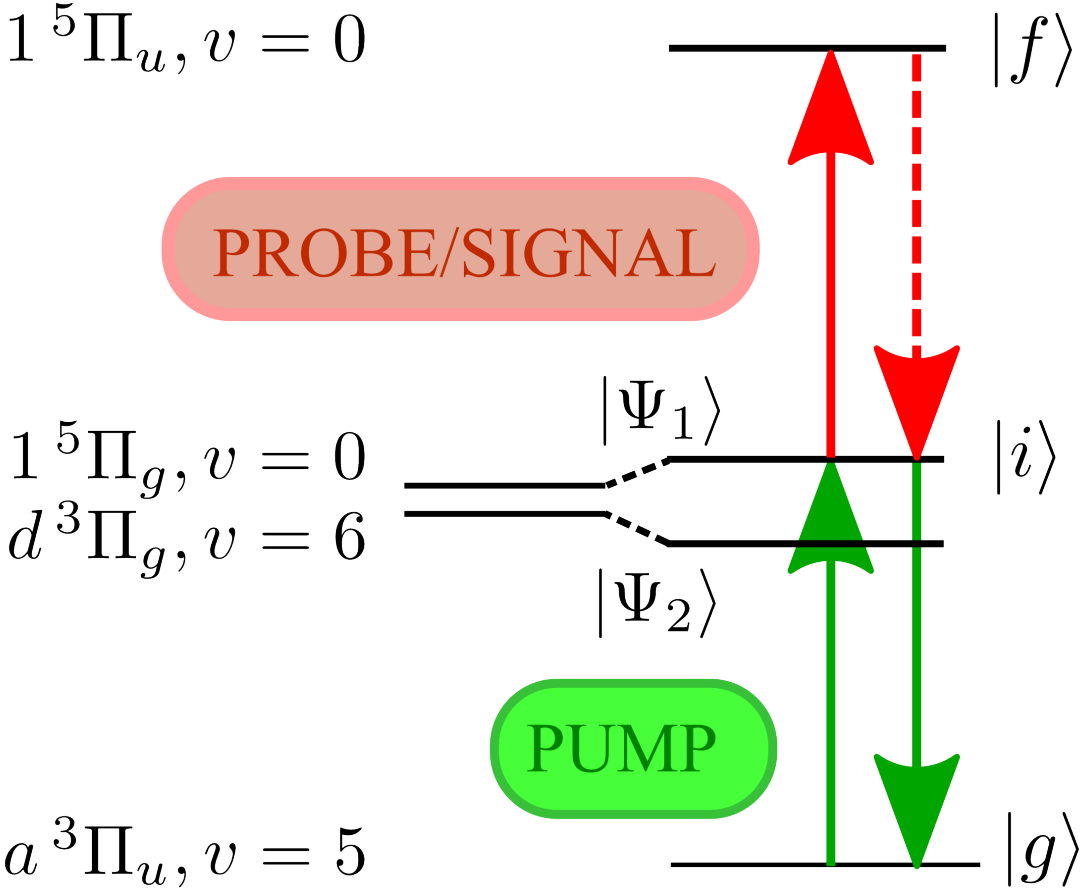
where $\sigma_{E,J;E,J'}$ and $\sigma_{E',J;E',J'}$ are the $J \to J'$ purely rotation-changing cross-sections within the E and E′ electronic states, resp., and $C_{E,E'}$ is the isolated-molecule E, $J \sim$ E′, J mixing coefficient.

W.M. Gelbart and K.F. Freed, Chemical Physics Letters 18, 470 (1973).

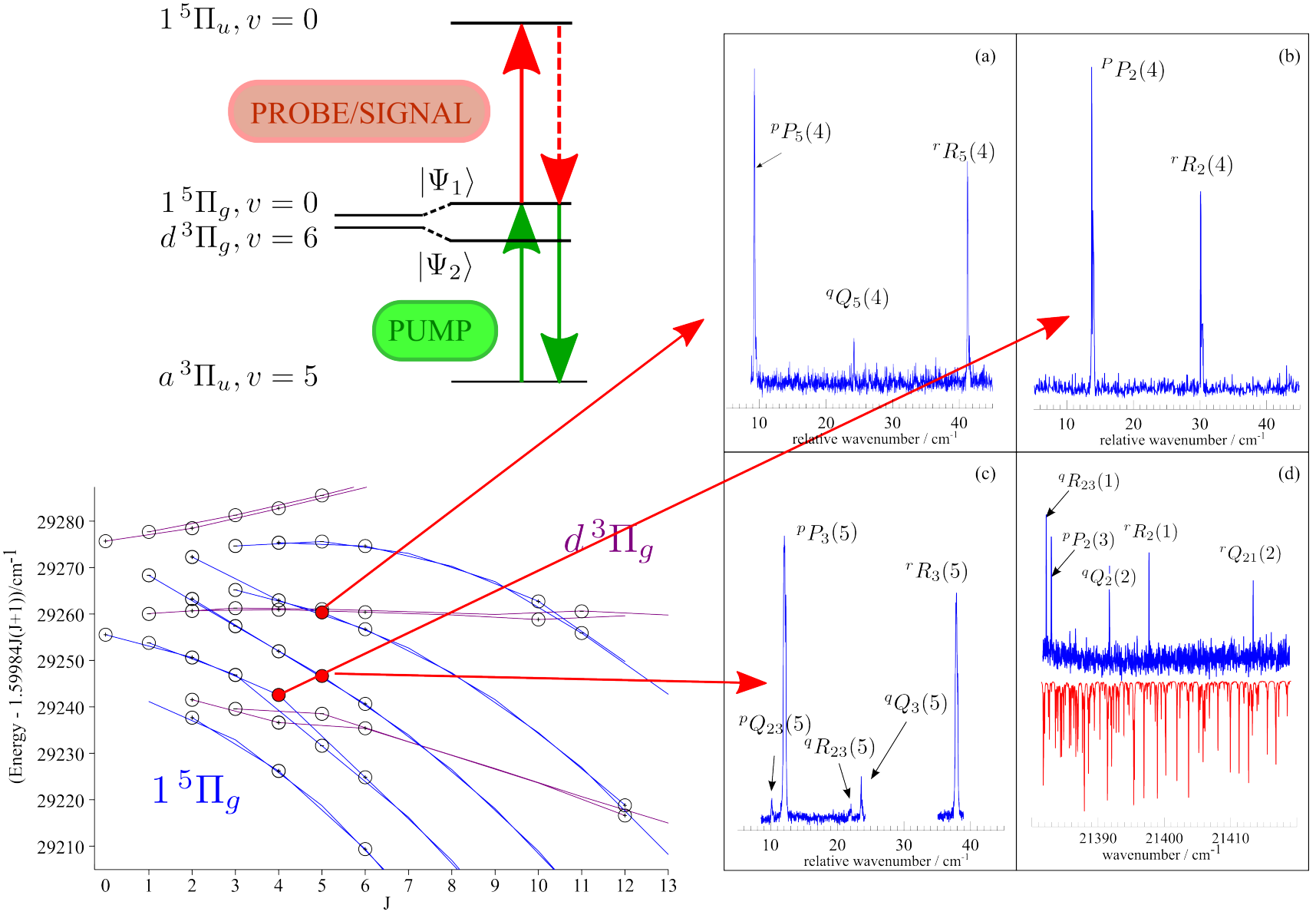
Quintet Character



First excited quintet state, the (1,0) band of 1 $^5\Pi_u$: PFOODR by UNFOLDED TC-RFWM



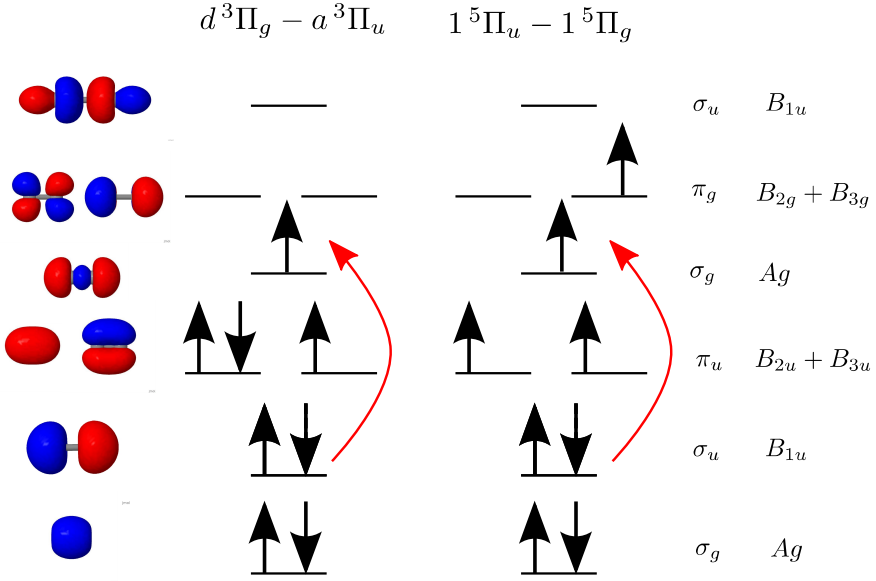
First excited quintet state, the (1,0) band of 1 $^5\Pi_u$: PFOODR by UNFOLDED TC-RFWM



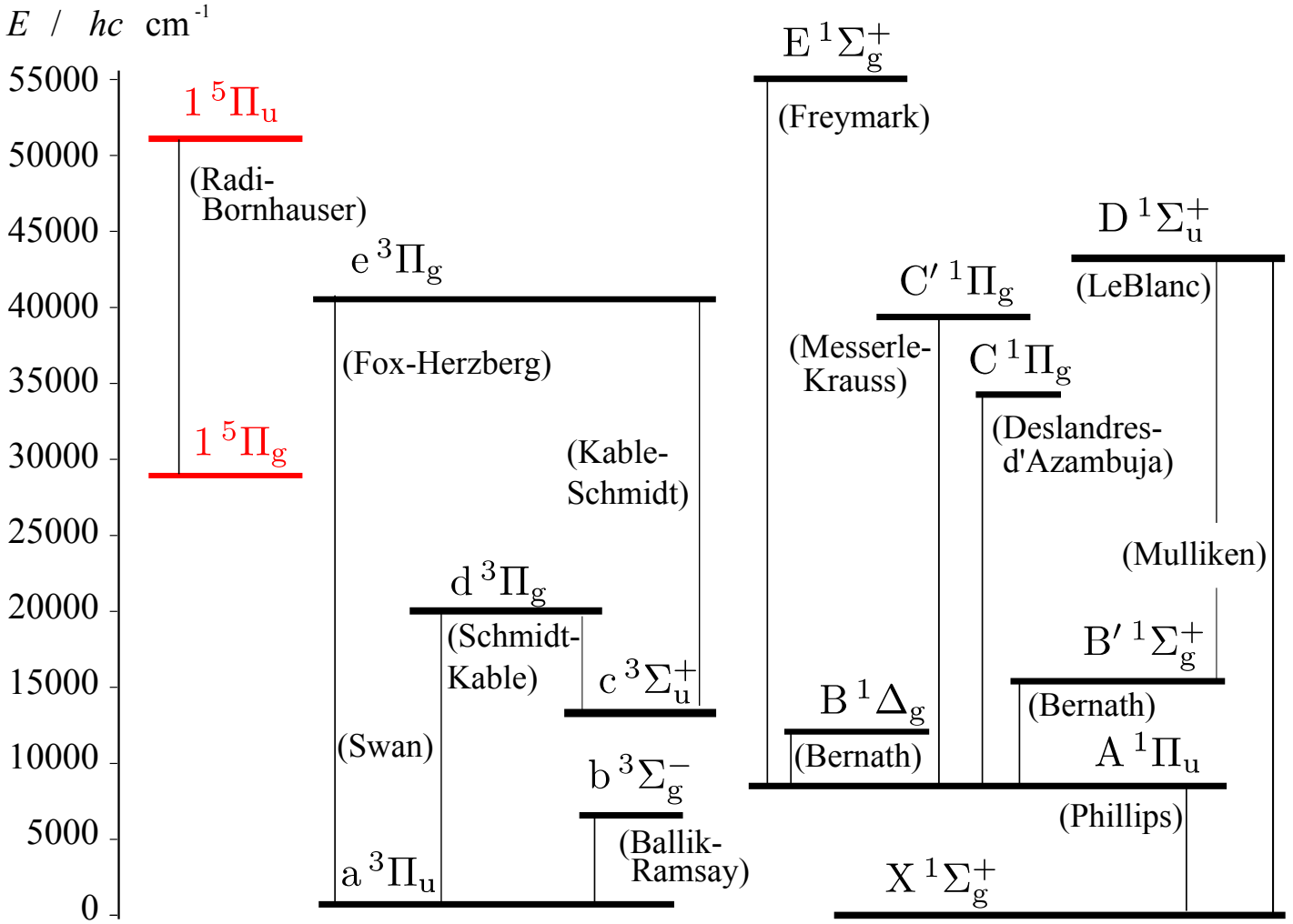
Molecular constants of the 1 $^5\Pi_u$ state

TABLE III. Optimized molecular constants for the 1 $^5\Pi_u$ state. For comparison, parameters for the 1 $^5\Pi_g$, d $^3\Pi_g$, and a $^3\Pi_u$ states are listed in addition. All values are given in cm^{-1}. T is relative to the a $^3\Pi_u$, $v = 0$ state. Uncertainties are one standard deviation.

Parameter	1 $^5\Pi_u$	1 $^5\Pi_g$ [a]	d $^3\Pi_g$ [b]	a $^3\Pi_u$ [b]
T_0	51 049.799 5(48)	29 258.592 2(48)	19 378.464 46(30)	0
B_0	1.219 05(21)	1.144 13(11)	1.745 569 5(20)	1.624 045 1(22)
A_0	8.198 3(37)	8.945 0(47)	−14.001 11(28)	−15.269 12(20)
λ_0	0.035 0(15)	−0.042 8(23)	0.033 03(20)	−0.154 90(25)
o_0	−0.034 3(19)	−0.074 4(39)	0.610 85(22)	0.675 39(20)
$D_0 \times 10^6$	10(1)	...	6.821 03(66)	6.450 68(84)

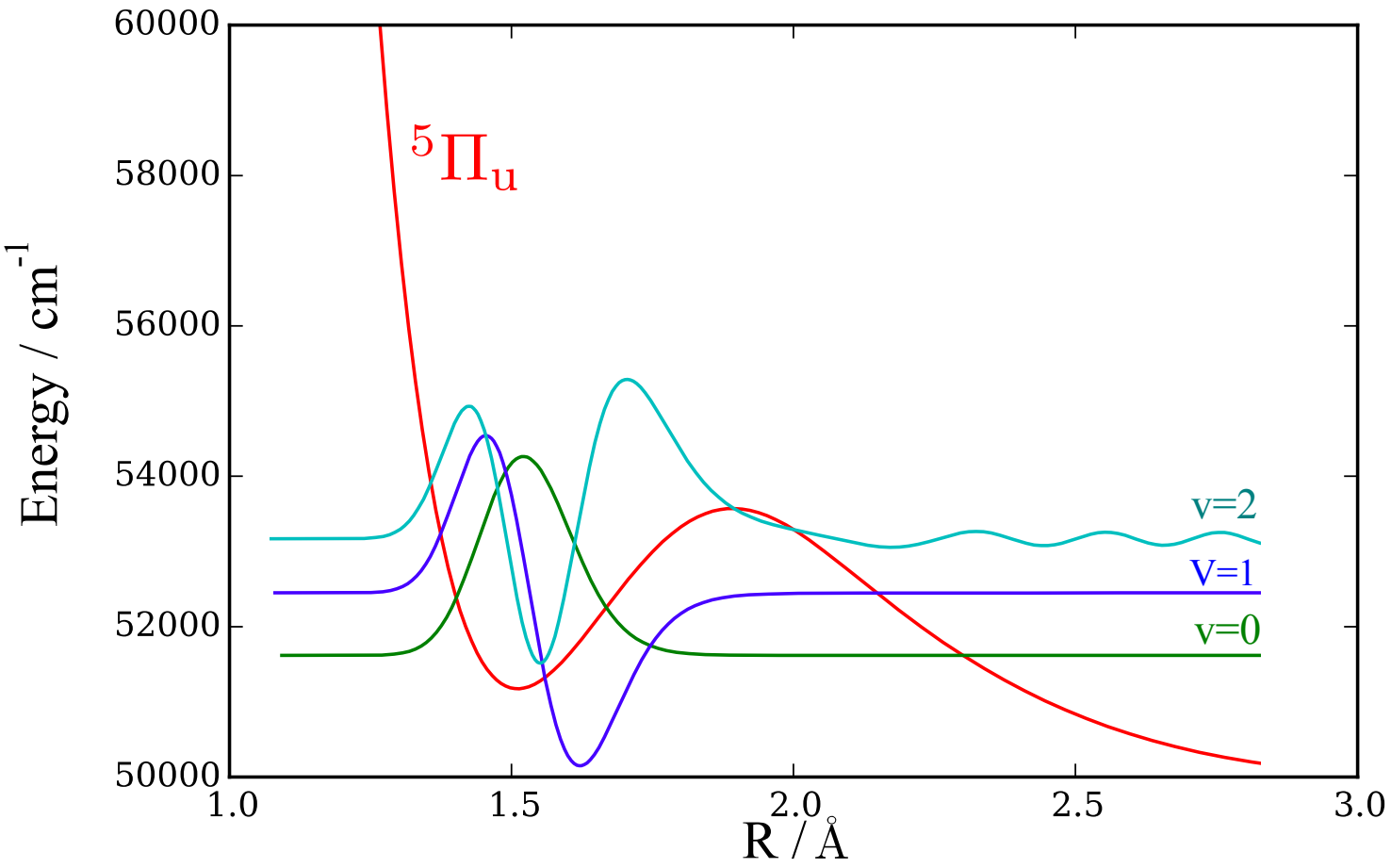


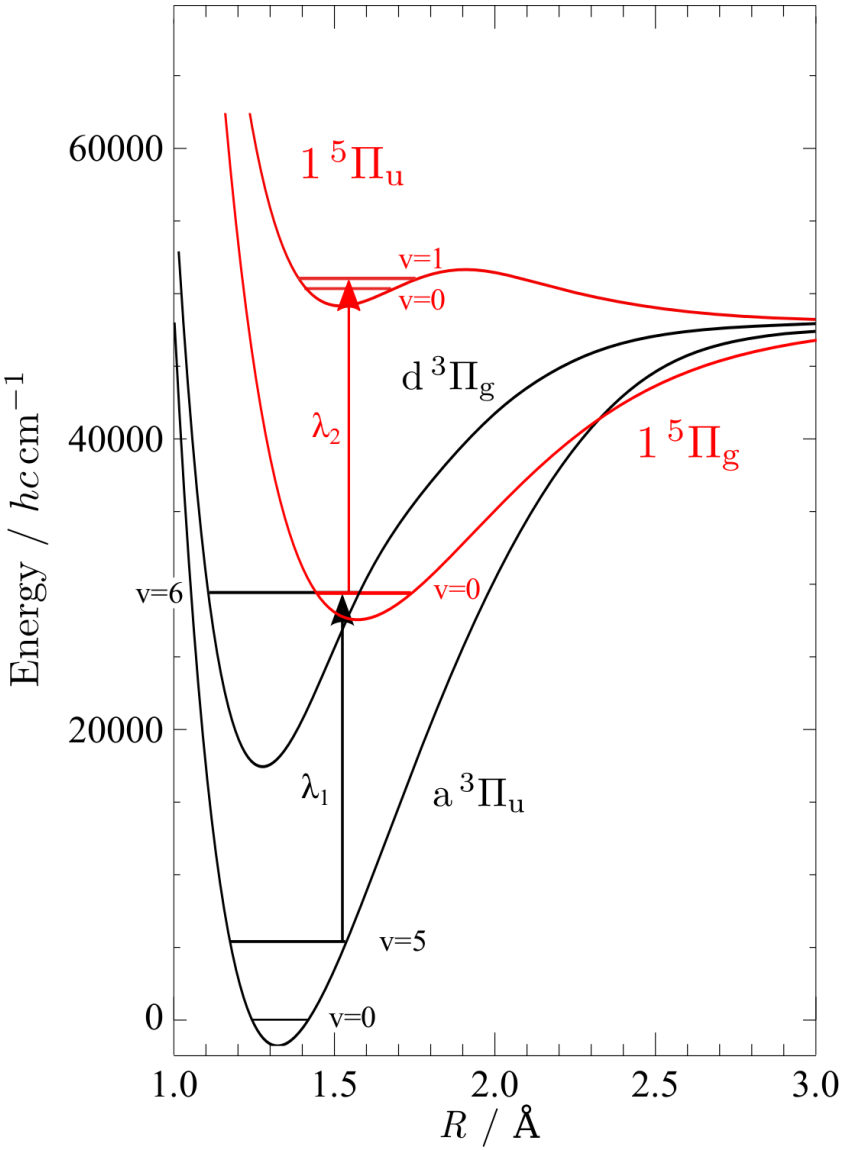
P. Bornhauser, R. Marquardt, C. Gourlaouen, G. Knopp, M. Beck, T. Gerber, J.A. van Bokhoven, and P.P. Radi, The Journal of Chemical Physics 142, 094313 (2015).



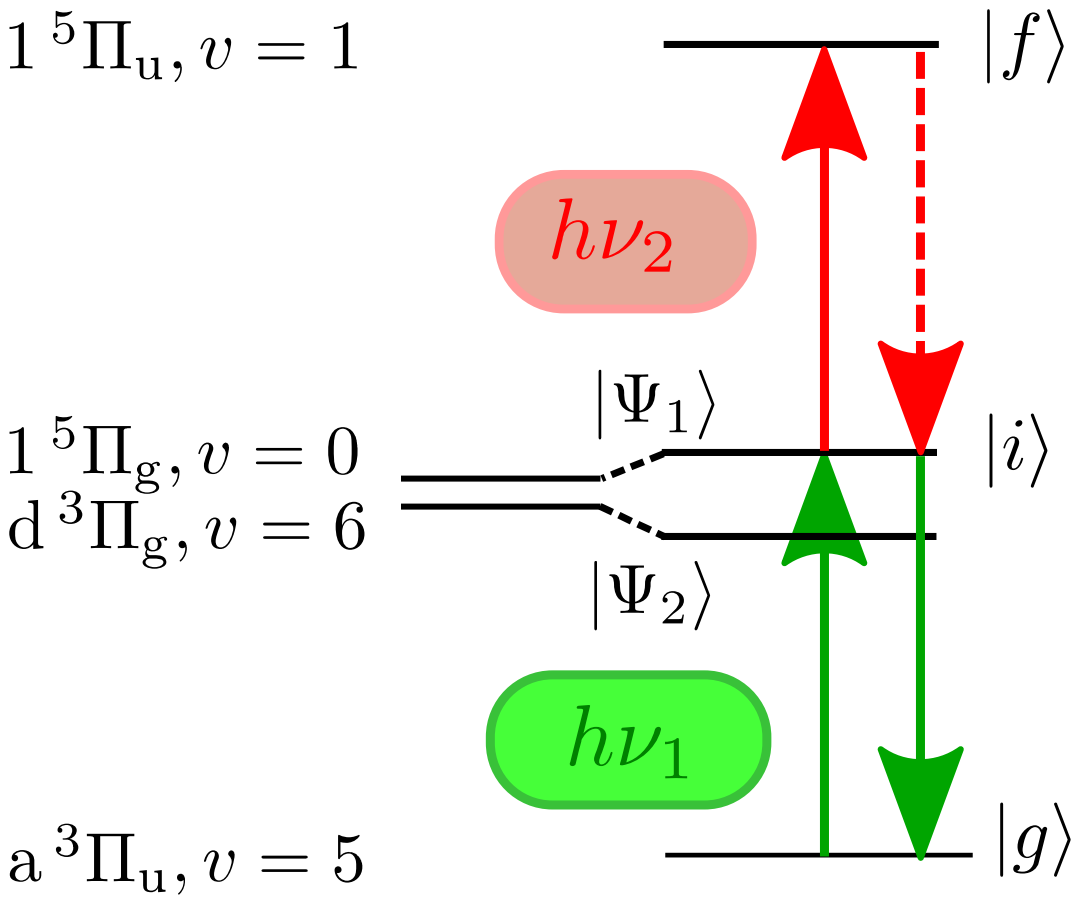
Journal of Chemical Physics 142, 094313 (2015)

1 $^5\Pi_u$ wavefunctions (ab initio)

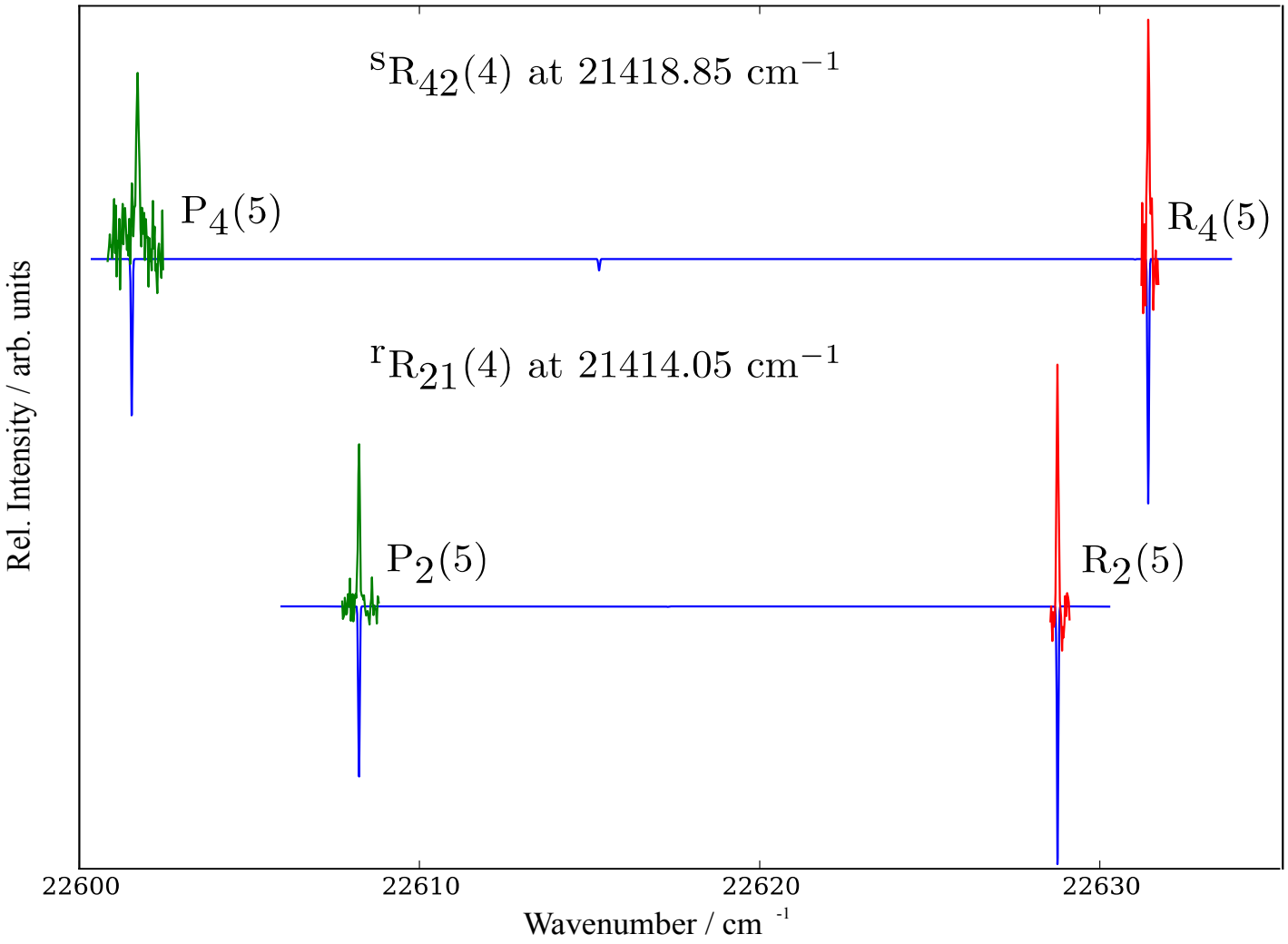



60000
40000
20000
0
Energy / hc cm^{-1}
1.0
1.5
2.0
2.5
3.0
R / Å
$1\,^5\Pi_u$
v=1
v=0
$d\,^3\Pi_g$
λ_2
$1\,^5\Pi_g$
v=6
v=0
λ_1
$a\,^3\Pi_u$
v=5
v=0

PFOODR of 1 $^5\Pi_u$, v=1

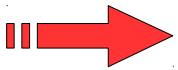


PFOODR of 1 $^5\Pi_u$, v=1



PFOODR of 1 $^5\Pi_u$, v=1

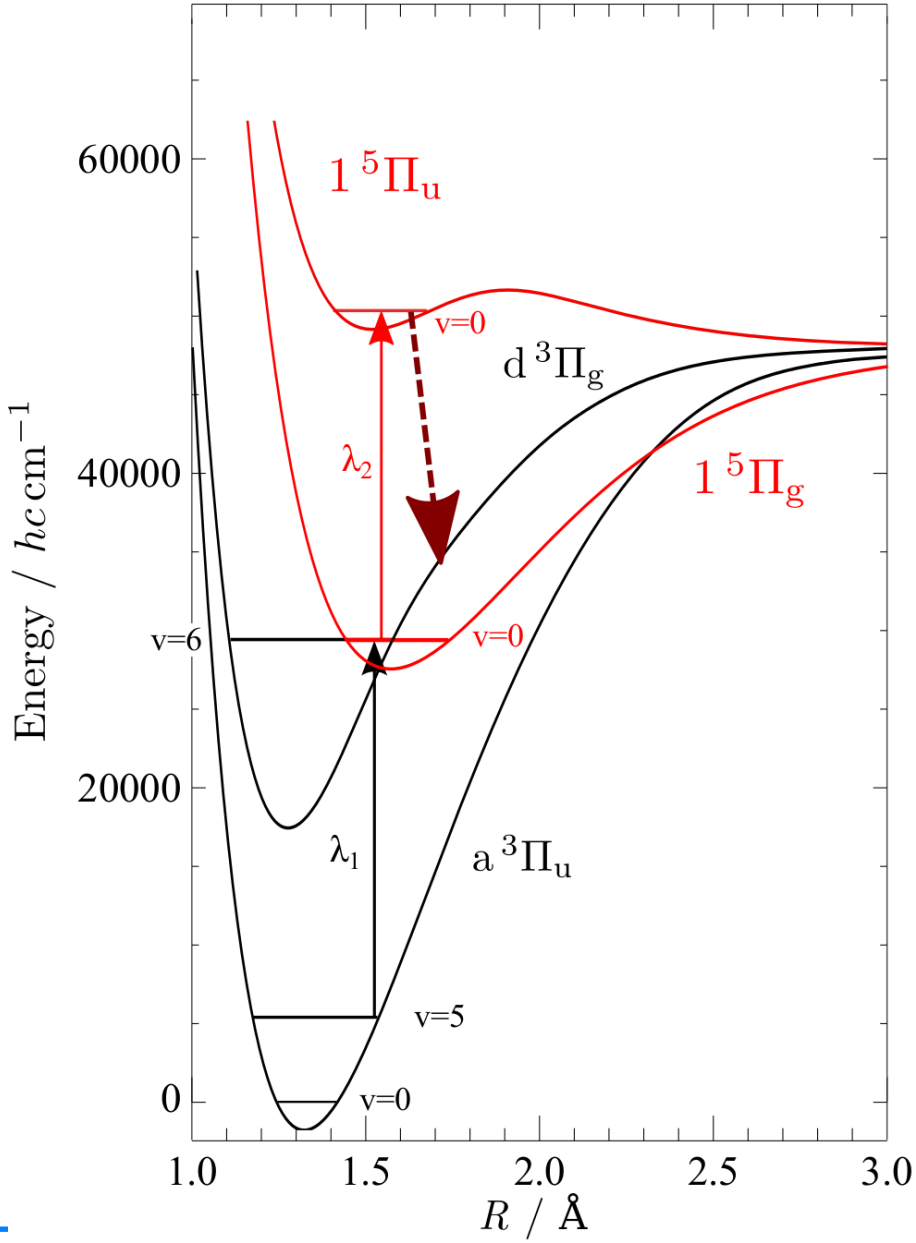
Upper Level $1\,^5\Pi_u$, v=1	Assignment $1\,^5\Pi_u$-$1\,^5\Pi_g$	Common intermediate level $1\,^5\Pi_g$, v=0	Pump $1\,^5\Pi_g$-a $^3\Pi_u$	Observed	Residuals
F2f(4)	(1,0)pP2f(5)	F2f(5)	(0,5)rR21(4)	22608.224	-0.0105
F2f(4)	(1,0)pP2f(5)	F2f(5)	(0,5)rR21(4)	22608.224	-0.0105
F2f(6)	(1,0)rR2f(5)	F2f(5)	(0,5)rR21(4)	22628.758	0.0131
F2e(3)	(1,0)pP2e(4)	F2e(4)	(0,5)rR21(3)	22606.600	-0.0184
F2e(5)	(1,0)rR2e(4)	F2e(4)	(0,5)rR21(3)	22622.443	-0.0015
F3f(6)	(1,0)rR3f(5)	F3f(5)	(0,5)rR32(4)	22628.846	0.005
F3f(4)	(1,0)pP3f(5)	F3f(5)	(0,5)rR32(4)	22604.367	0.015
F4f(6)	(1,0)rR4f(5)	F4f(5)	(0,5)sR42(4)	22631.430	0.0081
F4f(6)	(1,0)rR4f(5)	F4f(5)	(0,5)sR42(4)	22631.426	0.0041
F4f(4)	(1,0)pP4f(5)	F4f(5)	(0,5)sR42(4)	22601.563	-0.0067
F5e(5)	(1,0)rR5e(4)	F5e(4)	(0,5)sR53(3)	22631.864	-0.0115
F5e(3)	(1,0)pP5e(4)	F5e(4)	(0,5)sR53(3)	22601.240	-0.0231
F3e(1)	(1,0)qP3e(2)	F3e(2)	(0,5)qP32(3)	22611.363	0.0369



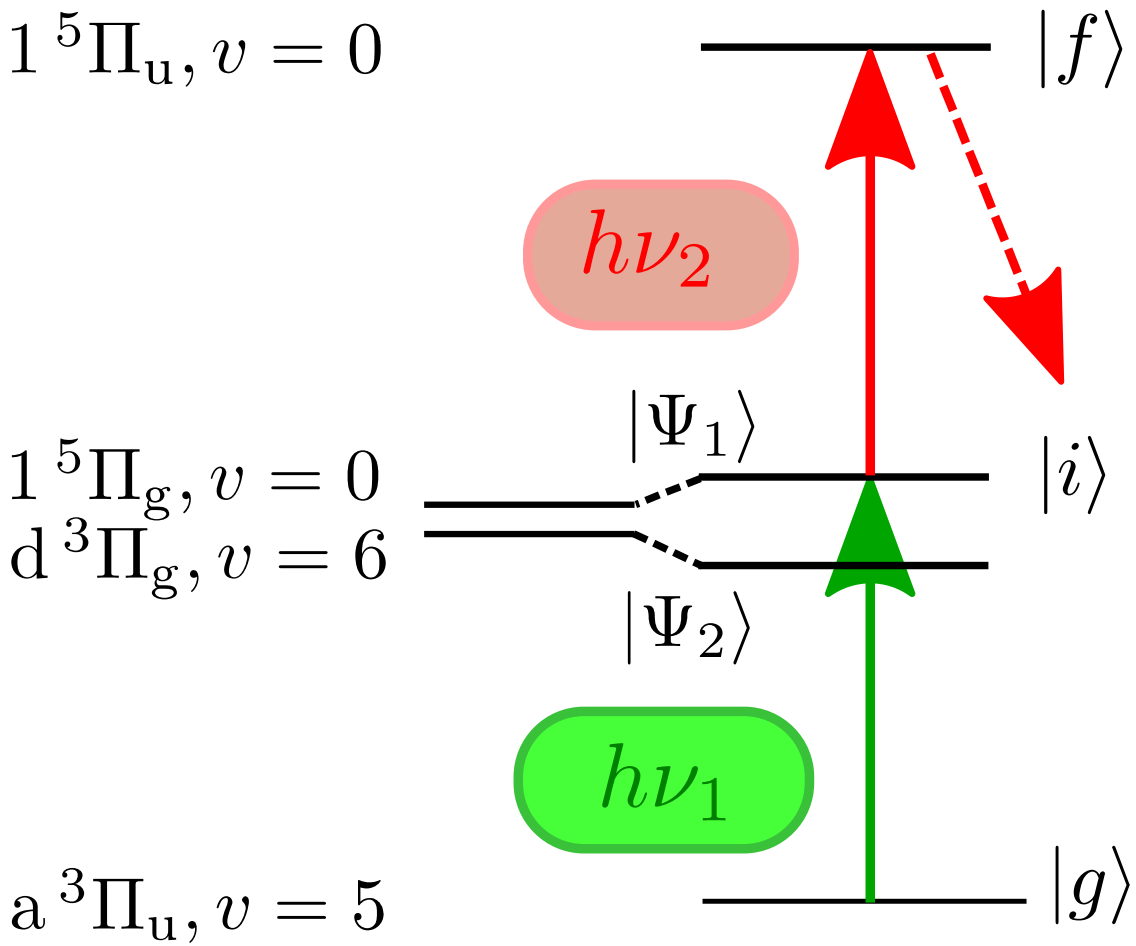
V_1=823.435(15)

State Parameter	v=1	v=0
T	51873.235(14)	51049.7995(48)
B	1.16588(46)	1.21905(21)
A	8.091(18)	8.1983(37)
λ	0.0252(45)	.0350(15)
o	-0.0441(59)	-.0343(19)
$D_0 \times 10^6$	-	10(1)

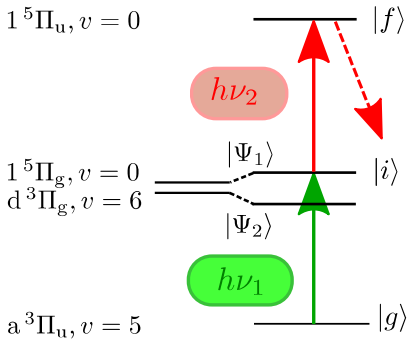
LIF from 1 $^5\Pi_g$?

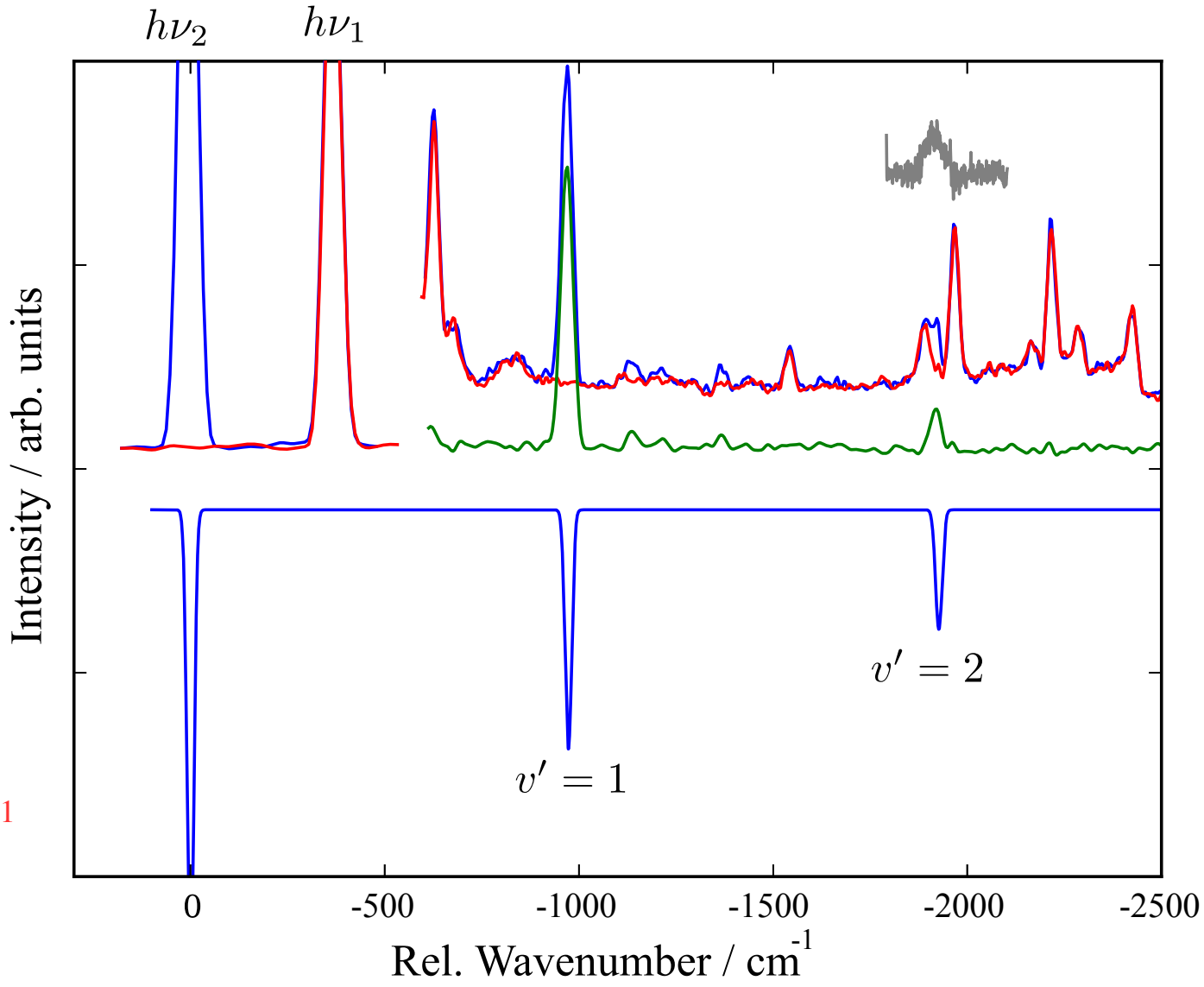


Perturbation Facilitated Optical-Optical Double-Resonance (PFOODR) and LIF



Vibrational structure of the 1 $^5\Pi_g$ state by PFOODR excitation and LIF

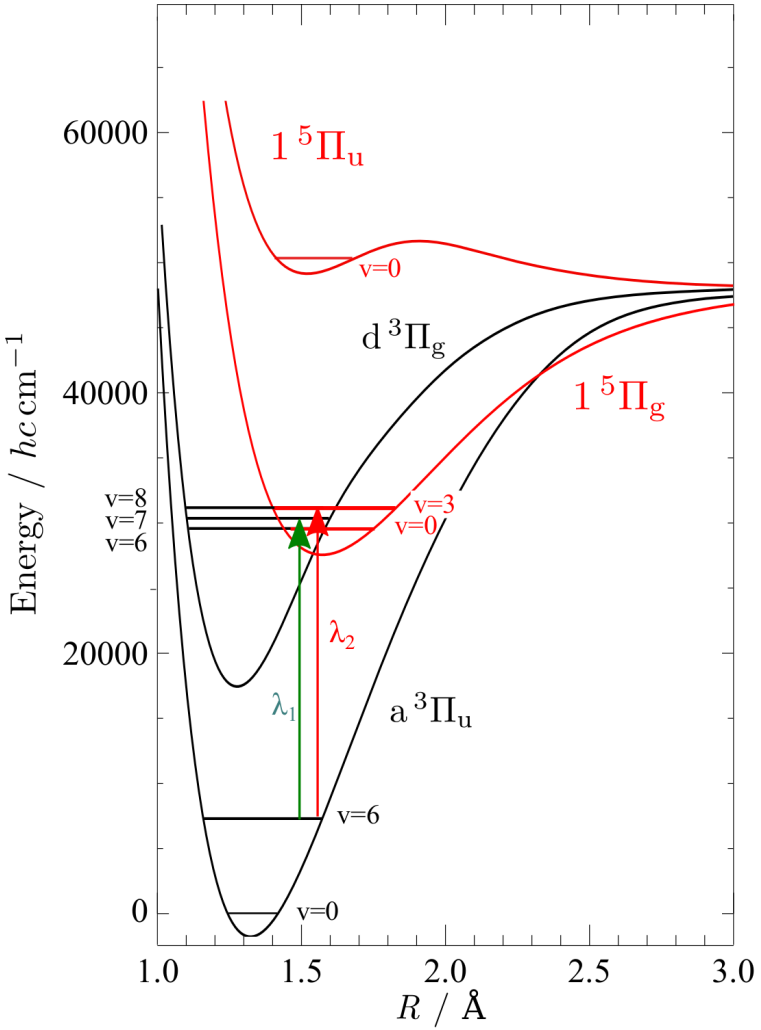




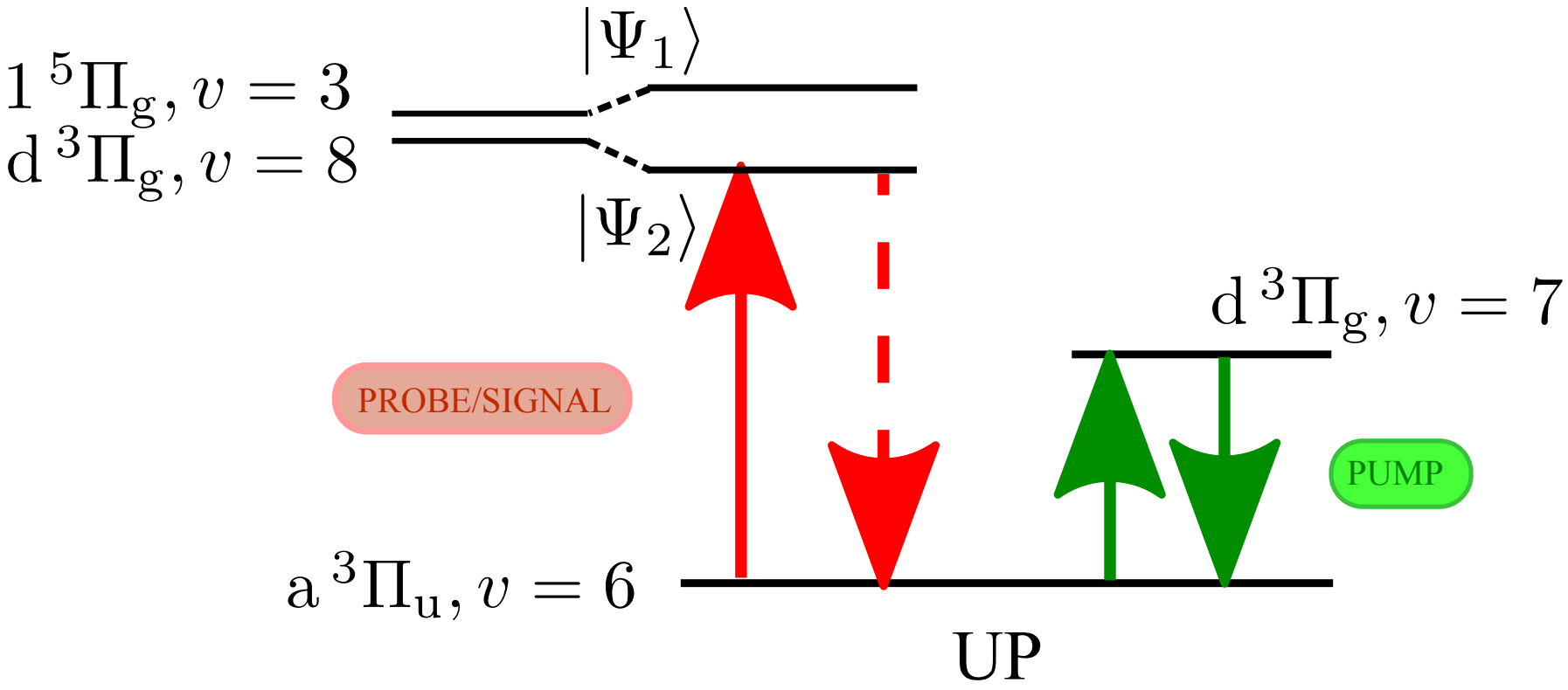
V_1=969.1(2) cm^{-1}

V_2=1913(1) cm^{-1}

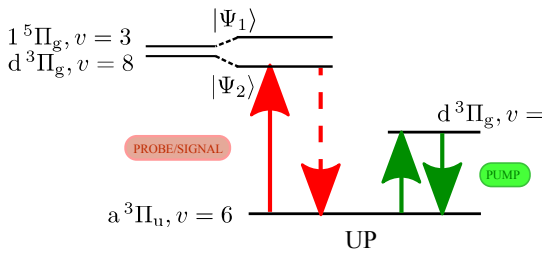
The origin of 1 $^5\Pi_g$, v=3 by depurturbation of d $^3\Pi_g$, v=8 ~ 1 $^5\Pi_g$, v=3

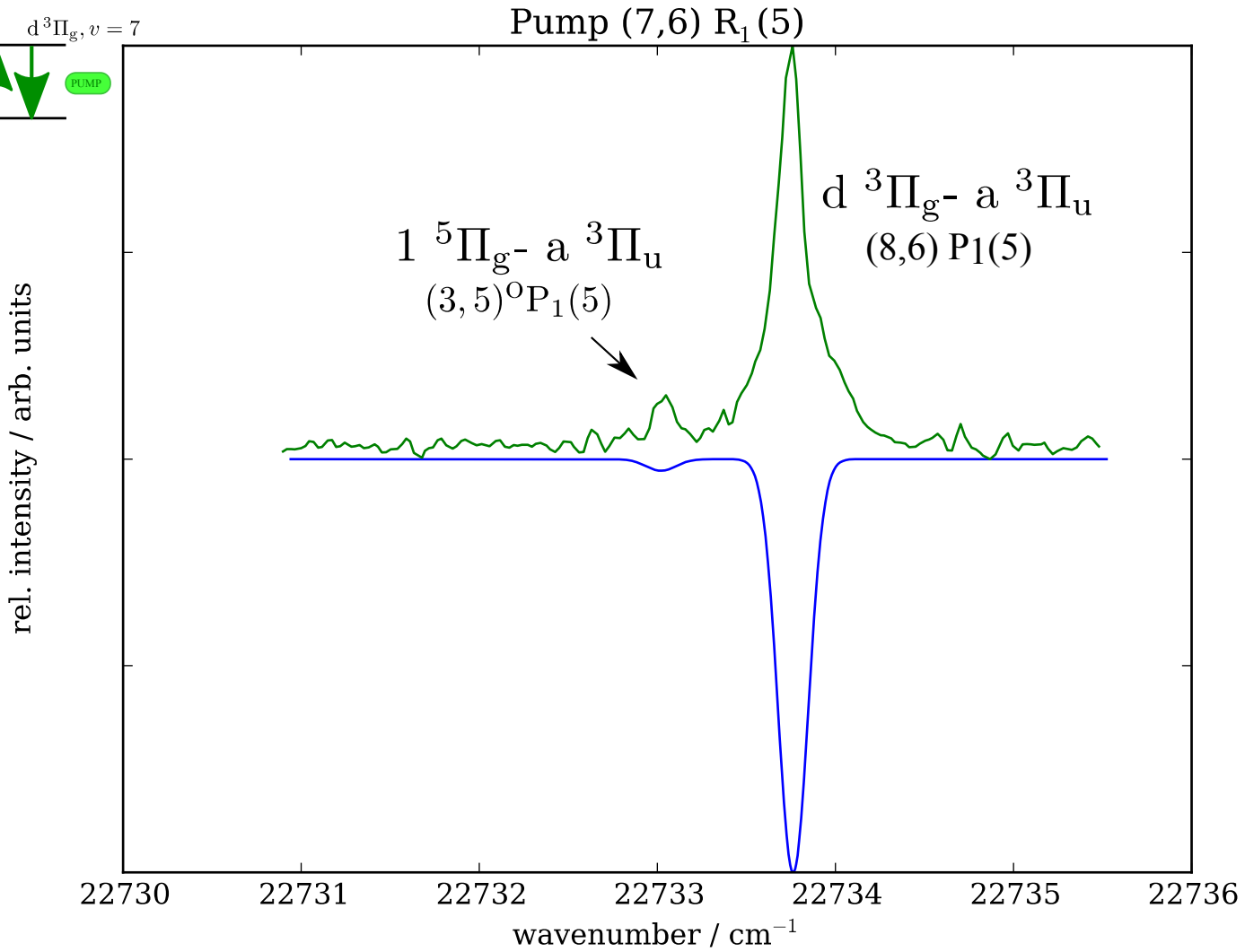


The origin of 1 $^5\Pi_g$, v=3 by depurturbation of d $^3\Pi_g$, v=8 ~ 1 $^5\Pi_g$, v=3

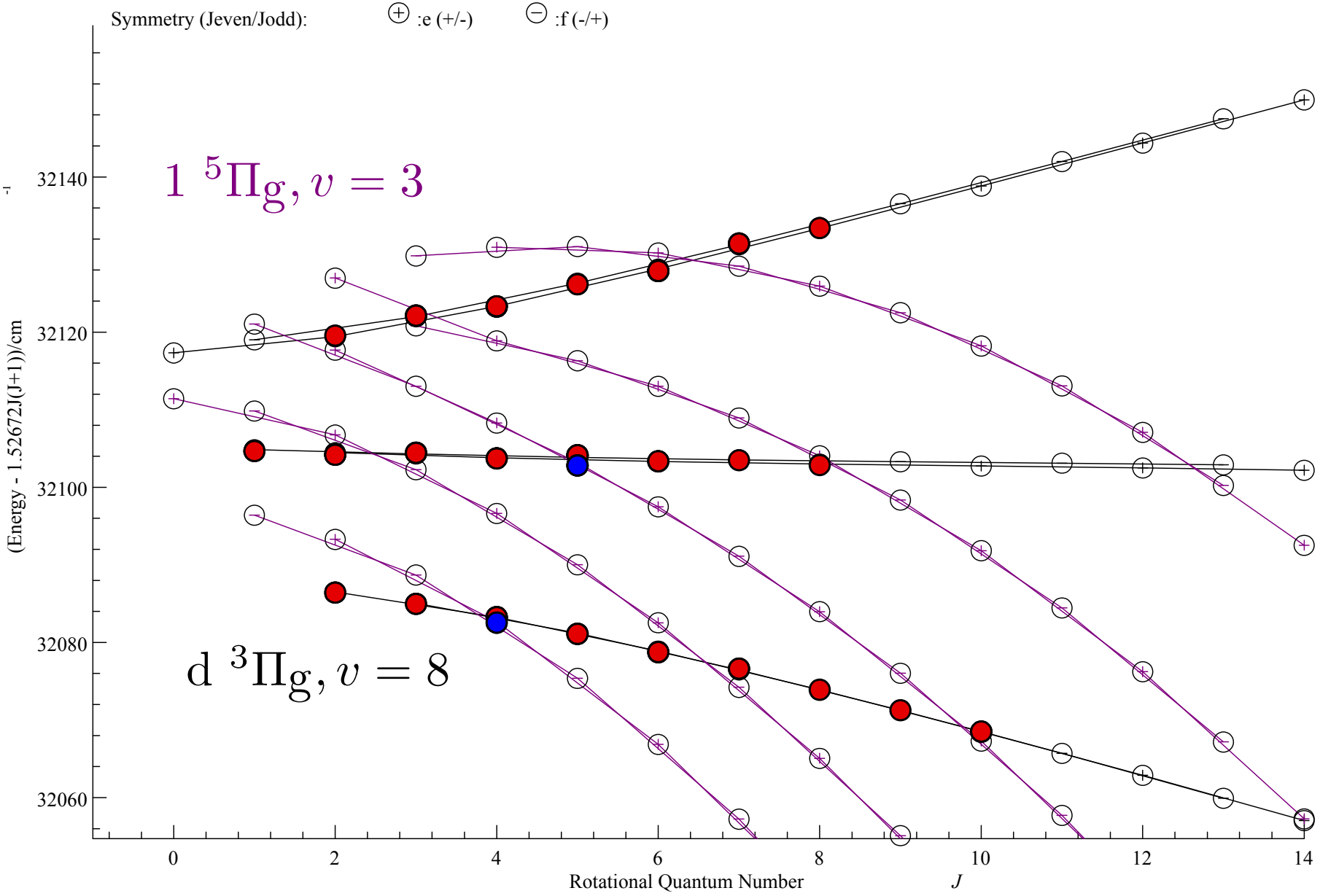


Deperturbation $\mathrm{d}\,^3\Pi_g, v = 8 \sim 1\,^5\Pi_g, v = 8$





Measured energy levels



The origin of 1 $^5\Pi_g$, v=3

TABLE I. TC-RFWM transitions (cm^{-1})

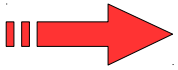
Upper Level	Assignment	Common lower level	Pump	Observed	Residuals
F1e(2)	(8,6) d-a qQ1f(2)	F1f(2)	(7,6)R1(2)	22747.49	-0.01
F1f(3)	(8,6) d-a pP1f(4)	F1f(4)	(7,6)R1(4)	22736.65	0.01
F1f(3)	(8,6) d-a rR1f(2)	F1f(2)	(7,6)R1(2)	22755.18	-0.01
F1e(4)	(8,6) d-a pP1e(5)	F1e(5)	(7,6)R1(5)	22733.75	-0.00
F1e(4)	(8,6) d-a rR1e(3)	F1e(3)	(7,6)R1(3)	22757.78	0.01
F1f(5)	(8,6) d-a pP1f(6)	F1f(6)	(7,6)R1(6)	22730.62	-0.00
F1f(5)	(8,6) d-a rR1f(4)	F1f(4)	(7,6)R1(4)	22760.26	0.00
F1e(6)	(8,6) d-a rR1e(5)	F1e(5)	(7,6)R1(5)	22762.81	0.00
F1f(7)	(8,6) d-a rR1f(6)	F1f(6)	(7,6)R1(6)	22765.84	-0.00
F1e(8)	(8,6) d-a rR1e(7)	F1e(7)	(7,6)R1(7)	22768.48	-0.01
F1f(9)	(8,6) d-a rR1f(8)	F1f(8)	(7,6)R1(8)	22771.26	0.03
F1e(10)	(8,6) d-a rR1e(9)	F1e(9)	(7,6)R1(9)	22774.16	-0.00
F2f(1)	(8,6) d-a pP2f(2)	F2f(2)	(7,6)R2(2)	22738.05	-0.02
F2e(2)	(8,6) d-a pP2e(3)	F2e(3)	(7,6)R2(3)	22735.01	0.02
F2f(3)	(8,6) d-a pP2f(4)	F2f(4)	(7,6)R2(4)	22732.30	0.00
F2f(3)	(8,6) d-a pP2f(4)	F2f(4)	(7,6)R2(4)	22732.30	-0.00
F2f(3)	(8,6) d-a rR2f(2)	F2f(2)	(7,6)R2(2)	22753.07	0.00
F2e(4)	(8,6) d-a rR2e(3)	F2e(3)	(7,6)R2(3)	22755.92	0.00
F2f(5)	(8,6) d-a pP2f(6)	F2f(6)	(7,6)R2(6)	22726.42	0.00
F2f(5)	(8,6) d-a rR2f(4)	F2f(4)	(7,6)R2(4)	22759.46	-0.00
F2e(6)	(8,6) d-a rR2e(5)	F2e(5)	(7,6)R1(5)	22762.35	0.01
F2f(7)	(8,6) d-a rR2f(6)	F2f(6)	(7,6)R2(6)	22765.49	-0.00
F2e(8)	(8,6) d-a rR2e(7)	F2e(7)	(7,6)R2(7)	22768.59	-0.01
F3e(2)	(8,6) d-a pP3e(3)	F3e(3)	(7,6)P3(3)	22731.47	0.00
F3f(3)	(8,6) d-a pP3f(4)	F3f(4)	(7,6)R3(4)	22728.11	-0.02
F3f(3)	(8,6) d-a rR3f(2)	F3f(2)	(7,6)R3(2)	22752.77	-0.00
F3e(4)	(8,6) d-a pP3e(5)	F3e(5)	(7,6)P3(5)	22725.13	-0.01
F3e(4)	(8,6) d-a pP3e(5)	F3e(5)	(7,6)R3(5)	22725.13	-0.00
F3e(4)	(8,6) d-a rR3e(3)	F3e(3)	(7,6)P3(3)	22756.61	0.00
F3f(5)	(8,6) d-a pP3f(6)	F3f(6)	(7,6)R3(6)	22721.82	-0.04
F3f(5)	(8,6) d-a rR3f(4)	F3f(4)	(7,6)P3(4)	22759.66	-0.04
F3e(6)	(8,6) d-a rR3e(5)	F3e(5)	(7,6)P3(5)	22763.29	-0.01
F3f(7)	(8,6) d-a rR3f(6)	F3f(6)	(7,6)P3(6)	22766.72	0.00
F3e(8)	(8,6) d-a rR3e(7)	F3e(7)	(7,6)P3(7)	22770.24	0.01
F1e(4)	(3,6) 1-a oP1e(5)	F1e(5)	(7,6)R1(5)	22733.03	-0.00
F3f(5)	(3,6) 1-a rR32f(4)	F2f(4)	(7,6)R2(4)	22758.16	0.01
F3f(5)	(3,6) 1-a pP32f(6)	F2f(6)	(7,6)R2(6)	22725.11	-0.00

State	Parameter	Value	Reference
$1\,^5\Pi_g$, v=3	T	32113.830(15)	32174[b]
	B	1.09932(73)	1.15361[b]
	A	9.0168(93)	
$d\,^3\Pi_g, v=8$	T	32102.6070(26)	32102.6713(90)[a]
	λ	0.0921(49)	0.046(12)[a]
$< d\,^3\Pi_1, v=8 \vert H_{so} \vert 1\,^5\Pi_1, v=3 >$		2.869(26)	

[a] experiment Ref.[1]

[b] theory, this work at the MRCI-F12 level of theory

TABLE II. Optimized molecular constants for the $1\,^5\Pi_g$, v=3 and the $d\,^3\Pi_g, v=8$ states. All values are in cm^{-1}. The origin, T is relative to the $a\,^3\Pi_u, v=0$ level. Numbers in parenthesis are one standard deviation.



V_1=969.1(2) cm^{-1}

V_2=1913(1) cm^{-1}

V_3=2854.708(20) cm^{-1}

Ref.[1]: A. Tanabashi, T. Hirao, T. Amano, and P.F. Bernath, The Astrophysical Journal Supplement Series 169, 472 (2007).

Ab initio

Parameter	a $^3\Pi_u$			
	pV6Z	F12-pCVQZ	exp.[a]	exp.[b]
T_0	0	0	0	0
r_e	1.3123	1.3119	-	1.311946(16)
w_e	1641.179(7)	1642.33(2)	1641.3463(55)	1641.341(23)
$w_e x_e$	-11.318(3)	-11.248(7)	-11.6595(19)	-11.6580(58)
$w_e y_e$	-0.0414(4)	-0.0547(10)	-0.00079(16)	-0.00083(41)
$w_e z_e$	0.00181(2)	0.00244(4)	-	0(fixed)
B_e	1.631404(28)	1.63231(7)	1.632355(78)	1.63235(4)
α_e	-0.016442(6)	-0.01645(2)	0.016582(63)	-0.01657(3)
$\gamma_e \times$	-0.00002750(43)	-0.000028(1)	-0.0000273(75)	-0.000027(5)
$\delta_e * 10^6$	0(fixed)	0.0(fixed)	-	0(fixed)
$D_e \times 10^6$	-6.431(33)	-6.43(9)	-	-
$\beta_e \times 10^6$	-0.015(5)	-0.02(1)	-	-
v_{max}	10	10	-	9
J_{max}	29	29	-	-
$\tilde{\nu}_{rms}$	0.018	0.047	-	-
v_0	0	0	0	0
v_1	1618	1620	1618.02244(53)	1618.02330(31)
v_2	3214	3216	3212.72793(96)	3212.72262(41)
v_3	4786	4790	4784.0688(31)	4784.1113(31)
v_4	6335	6340	6332.1364(51)	6332.1373(22)
v_5	7861	7867	7856.8175(32)	7856.8242(17)
v_6	9363	9371	9358.1565(40)	9358.1728(23)
v_7	10843	10851	10 836.1430(92)	10836.1550(45)
v_8	12298	12308	12 290.7997(29)	12290.903(27)
v_9	13731	13741	13 722.0897(43)	13722.1096(33)
v_10	15141	15152	-	-

Parameter	d $^3\Pi_g$			
	pV6Z	F12-pCVQZ	exp.[a]	exp.[b]
T_0	19430	19407	19378.46749(51)	19378.46446(30)
r_e	1.2657	1.2652	-	1.265122(32)
w_e	1783.69(4)	1788.61(2)	1788.45(33)	1789.094(21)
$w_e x_e$	-14.54(2)	-15.83(1)	16.87(19)	17.367(15)
$w_e y_e$	-1.020(6)	-0.701(4)	-0.259(36)	-0.1360(36)
$w_e z_e$	0.0270(5)	0.0020(3)	-0.0396(20)	-0.04878(25)
B_e	1.75372(6)	1.75514(4)	1.755408(92)	1.75542(9)
α_e	-0.01968(5)	-0.01989(3)	0.01960(13)	0.0196(1)
$\gamma_e \times$	-0.00022(2)	-0.00011(1)	-0.000144(39)	-0.00013(4)
$\delta_e * 10^6$	-69(2)	-81(1)	-80.6(3.1)	-82(3)
$D_e \times 10^6$	-6.55(6)	-6.55(4)	-	-
$\beta_e \times 10^6$	-0.29(2)	-0.28(1)	-	-
v_{max}	5	5	-	-
J_{max}	29	29	-	-
$\tilde{\nu}_{rms}$	0.024	0.014	-	-
v_0	0	0	0	0
v_1	1752	1755	1753.68228	1753.67514
v_2	3466	3471	3469.92021	3469.95054
v_3	5138	5146	5145.75261	5145.75774
v_4	6765	6775	6776.57731	6776.53584
v_5	8340	8353	8357.20451	8357.22024
v_6	9859	9877	9880.88731	9881.23954
v_7	11316	11340	11339.43361	11339.45724
v_8	12704	12737	12724.18751	12724.20684
v_9	14019	14064	14027.76251	14027.86054
v_10	15260	15319	15248.31851	15248.34484

ab initio

Parameter	$1\,^5\Pi_g$			$1\,^5\Pi_u$		
	pV6Z	F12-pCVQZ	exp.[a]	pV6Z	F12-pCVQZ	exp.[a]
T_0	29225	29308	29258.5922(48)	50932	51010	51049.7995(48)
r_e	1.5613	1.5606	-	1.5095	1.5084	-
w_e	994.12(1)	994.85(1)	-	907.7(1)	914.7(3)	-
$w_e x_e$	-9.743(4)	-9.853(5)	-	-22.0(2)	-25.53(9)	-
$w_e y_e$	-0.0085(6)	0.0116(7)	-	-6.60(5)	-6(fixed)	-
$w_e z_e$	-0.00121(3)	-0.00215(3)	-	0.0(fixed)	0.0(fixed)	-
B_e	1.15252(4)	1.15361(5)	-	1.224(2)	1.248(3)	-
α_e	-0.015428(10)	-0.01569(2)	-	-0.016(3)	-0.057(2)	-
$\gamma_e \times$	-0.0000866(6)	-0.000029(5)	-	-0.0138(8)	0.0(fixed)	-
$\delta_e * 10^6$	0.0(fixed)	-3.4(3)	-	0.0(fixed)	-0.0(fixed)	-
$D_e \times 10^6$	-6.12(5)	-6.12(6)	-	10.0(fixed)	0.0(fixed)	-
$\beta_e \times 10^6$	-0.063(8)	-0.063(9)	-	0.0(fixed)	0.0(fixed)	-
v_{max}	10	10	-	2	2	-
J_{max}	29	29	-	10	10	-
$\tilde{\nu}_{rms}$	0.027	0.032	-	0.069	0.217	-
v_0	0	0	0	0	0	0
v_1	975	975	969.1(2)	842	844	823.435(15)
v_2	1930	1931	1913(1)	1581	1583	-
v_3	2865	2866	2854.708(20)	-	-	-

33h 2h

Summary

Double-resonance investigations by Two-Color Resonant Four-Wave Mixing is advantageous to disentangle complex spectra:

- Characterization of perturbations in C_2
- Observation of dark states
- Intersystem crossing via gateway states to investigate states that cannot be accessed by direct optical transitions due to the stringent selection rule $\Delta S=0$
- Characterization of the first quintet-quintet band in C_2
- Ab initio at the MRCI level of theory with a pCV6Z basis set and comparison with MRCI-F12 including implicit correlation of the electrons

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